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1884 $\frac{30}{8}$ 1944

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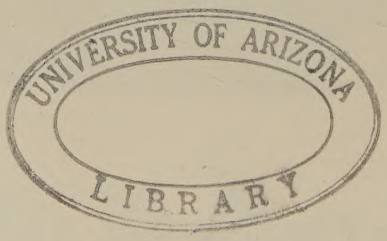

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UPPSALA 1944

Introduction.

On the 30th of August 1944, The Svedberg, Professor of Physical Chemistry at the University of Uppsala, attains the age of 60 years. His colleagues, pupils and other friends in scientific and industrial circles have decided not to let him pass this milestone as undisturbed by celebrations as he himself might have wished. All of us have reason to thank The Svedberg for what he has done for science, for our country and for ourselves. One often has a feeling that life does not give one sufficient opportunities of expressing gratitude. This is perhaps especially true in the daily routine of scientific and industrial research in the laboratory and in meetings where such research is planned and organised, which is the normal environment in which we have had our most frequent contact with The Svedberg. His birthday offers us, however, such an opportunity and the present volume is thus above all an expression of our gratitude. To this we add our congratulations; it is a great satisfaction to the friends of The Svedberg to see that a man who has been so exceptionally active in science from his early youth still possesses such abundant vitality, still finds new and fruitful fields for his initiative and work.

In planning this volume several factors have had to be taken into consideration. There has been no difficulty in obtaining contributions and financial support. The editorial committee can testify to the enthusiasm with which both have been offered; the only difficulty has been to limit the number of authors and the space allotted to each so that the volume should not become inconveniently large.

In a work of this kind one naturally wishes to touch upon as many as possible of the fields that interest the man to whom

170322

the volume is a tribute. In the case of THE SVEDBERG every field cannot be covered. Such a volume would contain not only scientific papers in chemistry, physics, biology, medicine and technology, but also essays on art and literature and perhaps other subjects as well. A man may cover all these fields with his mind and personality and make them harmonise; a book, even if it were written to mirror the interests of this man, would run the risk of becoming too heterogeneous; that, at least, is what we feared. The contributions have therefore been limited to the field of chemistry in its widest sense, including work in the borderland of the other sciences already mentioned and technology in particular to which THE SVEDBERG during the last years has devoted so much of his time and energy. The papers in botany represent a field which is SVEDBERG'S main recreation and to which he has also made remarkable contributions. Two of the papers are intended to give a picture of THE SVEDBERG'S scientific environment in Uppsala, both at an earlier period and in his present work at the Institute of Physical Chemistry.

We are fully aware that a volume dedicated to THE SVEDBERG and not containing any contributions from foreign countries is inadequate, to say the least. This book has been planned and written during the war when our communications with foreign countries are very uncertain. We know that most scientists abroad are engaged on work of immediate importance to their countries, and we have not considered it right to ask for contributions from them just now. In the list of authors there are only two exceptions to this rule, and in both cases the contributors have been able to collaborate with the Uppsala institute even in the present difficult circumstances. Swedish science has suffered in many ways from the war, but the situation has also raised many problems which have stimulated new research. This is especially true of the work on a great many chemical problems with industrial application. In this field THE SVEDBERG has made remarkable contributions, establishing close connections between academic science and industrial research to an extent unprecedented in this country. A number of contributions from industrial research laboratories emphasize the enthusiastic response to SVEDBERG'S initiative.

We hope that this volume will to a certain extent give a cross section of Swedish activities in chemical research during these difficult years, and that it will show how Swedish scientists, like The Svedberg himself, have tried to make the best of the situation; from this point of view the book may perhaps also serve as an historic document.

A large number of contributions originate from The Svedberg's own institute. The authors of these papers wish to express here their deep gratitude to the Director of the institute for the unfailing interest he has always shown in their work, for the fertile ground and stimulating atmosphere which he has created in the laboratory and for the ideal working conditions, also as regards material resources, for which his institute is famous. Most of these authors have also enjoyed the privilege of having The Svedberg as teacher for a longer or shorter period, a period which has been of decisive influence on their scientific careers. It is a particularly great pleasure to them to have this opportunity of expressing their gratitude.

The Svedberg has once said that there is hardly anything which makes him happier than planting a young seedling and watching it grow. Many of his friends have had the pleasure of sharing this happiness with him in the "botanical gardens" which he has created around his cottage at Vretaudd and on his summer islands on the West coast. We hope that he will also find in this book some passages which may awaken in him a feeling of the same kind, a feeling that what he once planted has grown and developed.

Uppsala and Stockholm June 10th, 1944.

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A Recording Surface Balance of the Wilhelmy-Dervichian Type.

By Kjell J. I. Andersson, Stina Ställberg-Stenhagen and Einar Stenhagen.

From the Institute of Physical Chemistry, the Institute of Physiology and the Institute of Medical Chemistry, University of Uppsala.

The continuous automatic recording of force-area curves in monolayer work has several advantages over the ordinary method, in which the monolayer is compressed stepwise and the surface pressure measured after each compression. With stepwise compression it is quite easy, even in very careful work, to miss slight discontinuities in the curves. If many points on the curves are to be obtained, the run takes a considerable time, and it is impossible to obtain reliable results from monolayers which collapse easily or slowly dissolve in the substrate. It is especially difficult to obtain the steep high-pressure part of the force-area curves characteristic of many liquid condensed and solid monolayers.

Dervichian (1, 2) has constructed an automatically recording surface balance on Wilhelmy's principle (3, 4). Surface balances of this type have been constructed at the Institute of Physical Chemistry and the Institute of Physiology at Uppsala, and we intend to give a description of the most recent instrument which shows improvements in many respects over Dervichian's original apparatus.

Principle of the Method.

A thin rectangular glass plate is suspended vertically from one arm of a balance in such a way that it is partly immersed in the substrate on whose surface the monolayer is to be spread (Fig. 1). If b is the width of the plate and t its thick-

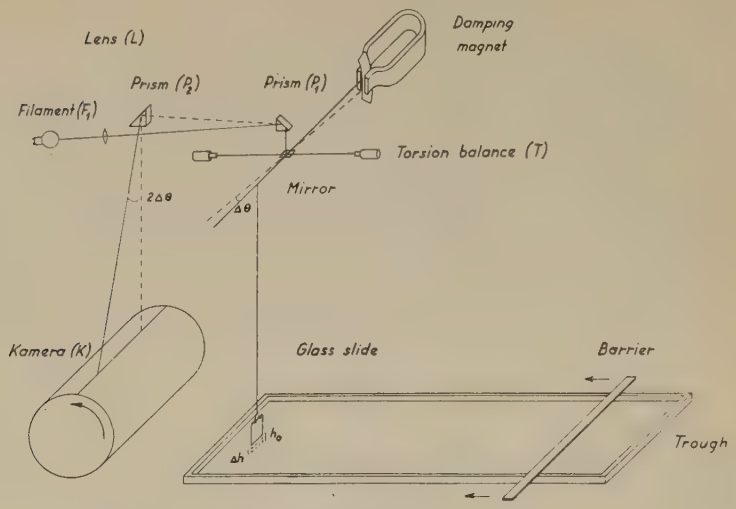

Fig. 1.

ness, its perimeter is $2(t + b)$. If the surface tension is denoted by γ (dynes per cm) and the angle of contact by α, the vertical pull of the surface tension on the plate is

$$2\gamma(t + b)\cos\alpha.$$

This force is counteracted by the force of buoyancy equal to $g \cdot d \cdot t \cdot b \cdot h$, where g is the acceleration of gravity, d the density of the substrate and h the depth of immersion of the slide. If G is the weight of the dry slide and its suspension, and l_1 the balance arm, the torque acting on the balance is equal to

$$l_1[g \cdot G + 2\gamma(t + b)\cos\alpha - g \cdot d \cdot t \cdot b \cdot h]$$

In the present case a torsion balance is used and at equilibrium this torque is counteracted by the torque $k \cdot \theta$ of the balance, where k is a constant and θ the angle of rotation of the mid-point of the torsion wire relative to the supports. With no film present we have $\gamma = \gamma_0$, $\theta = \theta_0$ and $h = h_0$. On the assumption that the contact angle is equal to zero the following relation holds

$$k \cdot \theta_0 = l_1[g \cdot G + 2\gamma_0(t + b) - g \cdot d \cdot t \cdot b \cdot h_0] \qquad (1)$$

Suppose now that a monolayer is spread on the surface and compressed by a glass barrier. This lowers the surface tension to γ_f and the slide rises, and this deflects the beam of the balance. If the angle of contact is still zero and the new values of θ and h are θ_f and h_f respectively, we have for the new equilibrium

$$k \cdot \theta_f = l_1 \left[g \cdot G + 2\gamma_f (t + b) - g \cdot d \cdot t \cdot b \cdot h_f \right] \qquad (2)$$

In order to calibrate the balance we remove a weight w from the beam of the balance. The weight is normally carried at a distance l_2 from the centre of rotation by the same arm as carries the suspension of the slide. This changes θ to θ_w and h to h_w. If no film is present $\gamma = \gamma_0$, and at the new equilibrium we have

$$k \cdot \theta_w = l_1 \left[g \cdot G + 2\gamma_0 (t + b) - g \cdot d \cdot t \cdot b \cdot h_w \right] - l_2 \cdot g \cdot w \qquad (3)$$

Subtraction of eq. (2) from eq. (1) gives

$$k (\theta_0 - \theta_f) = l_1 \left[2 (t + b) (\gamma_0 - \gamma_f) - g \cdot d \cdot t \cdot b (h_0 - h_f) \right] \qquad (4)$$

where $\gamma_0 - \gamma_f = \Delta\gamma$ is equal to the film pressure. Similarly, subtraction of eq. (3) from eq. (1) gives

$$k (\theta_0 - \theta_w) = - l_1 \cdot g \cdot d \cdot t \cdot b (h_0 - h_w) + l_2 \cdot g \cdot w \qquad (5)$$

For small deflections of the balance both $(\theta_0 - \theta_f)$ and $(h_0 - h_f)$ are proportional to the change in position s of the beam of light on the recording paper. (The errors involved in this assumption are discussed later.) The same holds for $(\theta_0 - \theta_w)$ and $(h_0 - h_w)$, and we may therefore write

$$k (\theta_0 - \theta_f) = k' \cdot s_f, \quad g \cdot d \cdot t \cdot b (h_0 - h_f) = k'' \cdot s_f$$

$$k (\theta_0 - \theta_w) = k' \cdot s_w, \quad g \cdot d \cdot t \cdot b (h_0 - h_w) = k'' \cdot s_w$$

Eq. (4) and (5) now become

$$k' \cdot s_f = l_1 \left[2 (t + b) \Delta\gamma - k'' \cdot s_f \right] \qquad (6)$$

$$k' \cdot s_w = - l_1 \cdot k'' \cdot s_w + l_2 \cdot g \cdot w \qquad (7)$$

Elimination of k' and k'' between eq. (6) and (7) and solving for $\Delta\gamma$ gives

$$\Delta\gamma = \frac{l_2 \cdot s_f \cdot w \cdot g}{2 \cdot l_1 \cdot s_w (t + b)}. \qquad (8)$$

The above relations only hold if the angle of contact is zero. There is no difficulty in obtaining this contact angle with a clean glass or quartz slide when the slide is rising (receding contact angle), *i. e.* when the film is continually compressed and as a result the film pressure rises. On the other hand, if the monolayer is expanded the pressure falls and the slide moves downwards. In this case it is not always possible to maintain a contact angle equal to zero. As a rule, therefore, surface balances utilizing the WILHELMY principle are not suitable for the study of the behaviour of monolayers on expansion.

Description of Apparatus.[1]

Thermostat.

For precise monolayer work it is necessary to be able to control the temperature of the film within very narrow limits. The thermostat used by us (see Figs. 2 and 3) allows the monolayer to be kept at any temperature between zero and + 55° C with variations less than 0.1°. A double-walled box of sheet copper (thickness 1 mm), having the inside dimensions 65 × 36 × 44 cm houses the trough. Water from a tank is circulated in the space (2 cm) between the walls of the box proper and of the lid, as is evident from the photograph shown in Fig. 2. The thermostat is thermally isolated by a layer of cork (2.5 cm thick) between the copper box and the outer box of "masonite" board. The lid is covered with masonite only. The tank is equipped with electrical heaters for work at higher temperatures, and a refrigerating system (Frigidaire 1/5 h. p.) for lower temperatures. Both heating and cooling systems are controlled by an adjustable electrical contact thermometer in the tank. The water (tank and thermostat box together hold 60 litres) is pumped from the tank through the thermostat

[1] Complete instruments according to this specification are made by *L. K. B.-Produkter Fabriksaktiebolag*, Alvik, Stockholm.

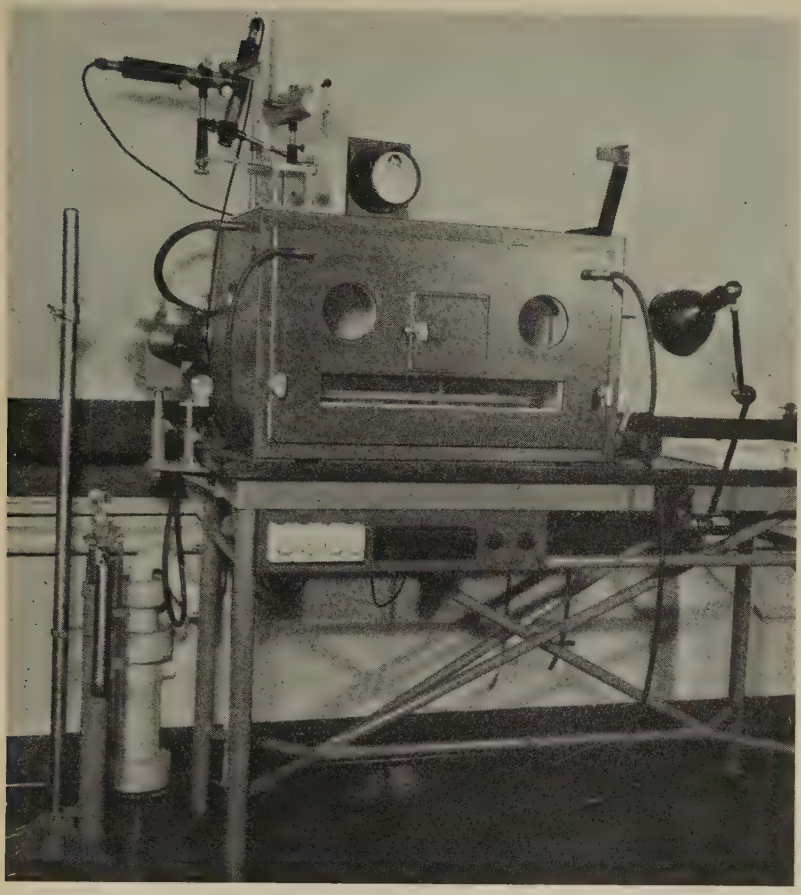

Fig. 2.

box by a small centrifugal pump. The water of the tank itself is effectively stirred by a separate stirrer.

An important detail of the thermostat system consists of a serpentine glass tube immersed in the substrate. Part of the water from the tank passes through this tube, which has an internal diameter of 6 mm and a length of 2 metres. The thermostat box has a number of holes, 2 cm in diameter, for electrical and mechanical connections of various kinds. In addition to the windows, the lid has a small square door for spreading purposes. The height of the thermostat allows a surface balance of the LANGMUIR-ADAM (horizontal) type to

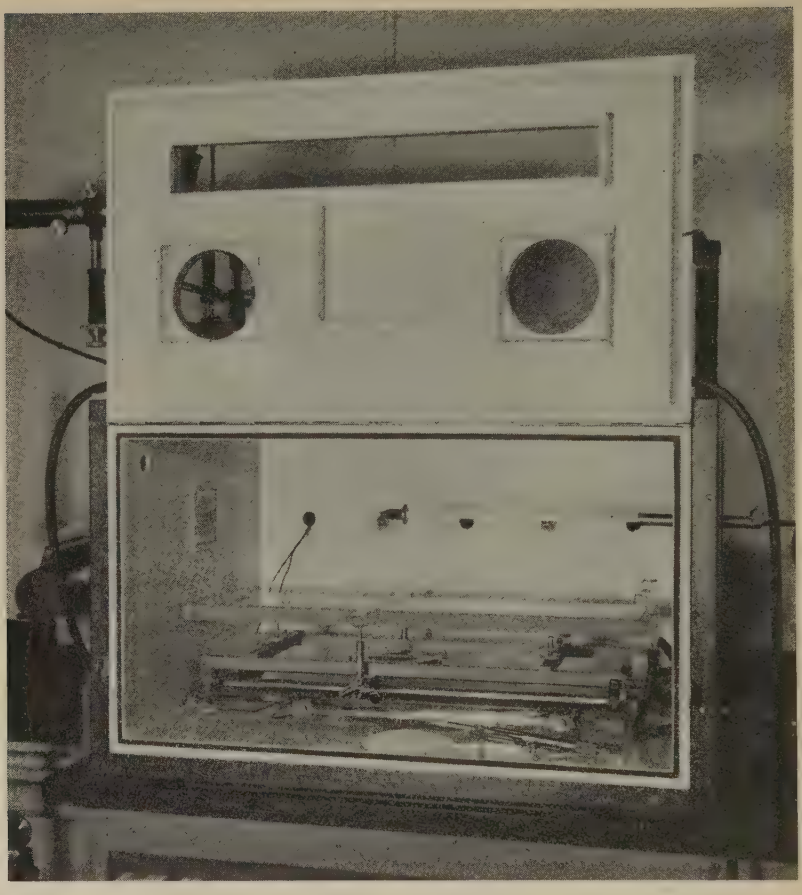

Fig. 3.

be used alternatively with the Wilhelmy-Dervichian (vertical) equipment. In order to allow control of the adjustment of the Langmuir-Adam balance by optical methods, the left side of the thermostat box has a glass window.

Polonium Electrode Carrier.

To allow surface potentials to be measured the right hand end of the thermostat carries the bearing for a polonium electrode carrier, the construction of which is shown in Fig. 4. The electrode holder H is made of ebonite and is fixed to the end of a rod R of square cross-section by the screw S.

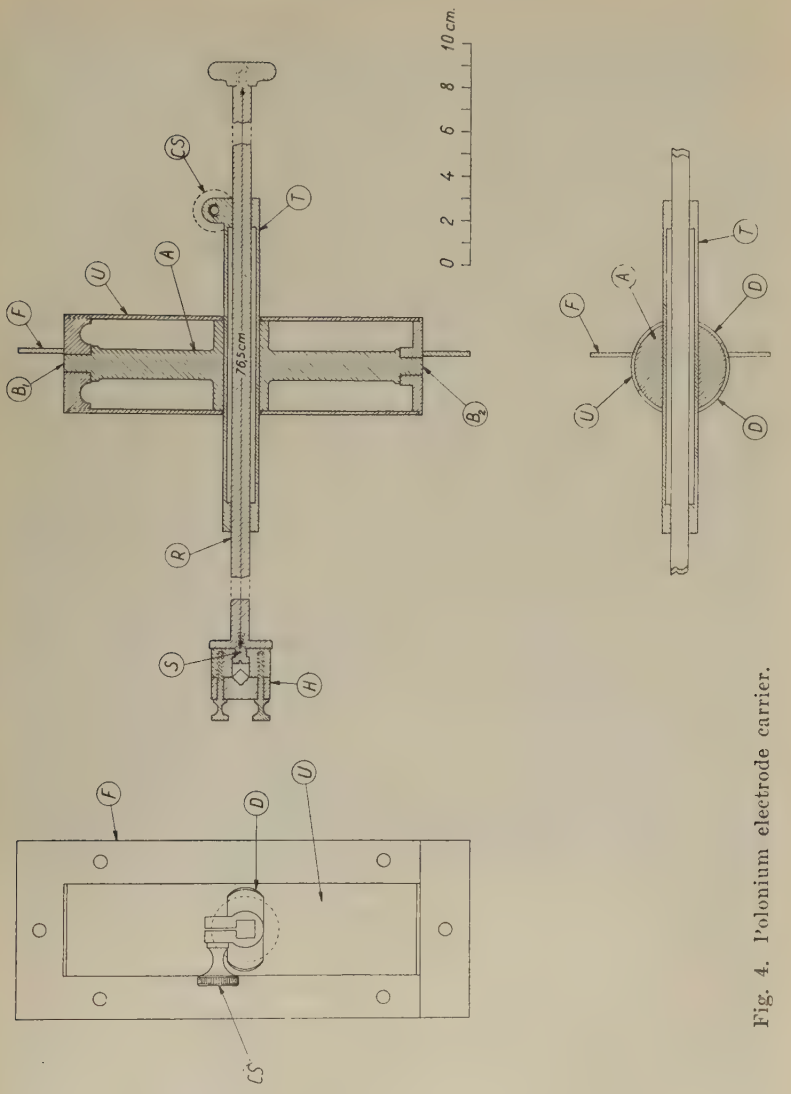

Fig. 4. Polonium electrode carrier.

The holder may be rotated around the axis of the rod. This allows the electrode to be moved out of the way of the barriers when the surface is being cleaned. The rod R slides in the tube T, and may be fixed in any position by the clamping screw CS. The tube T is fixed to the cylindrical part A, which may be rotated inside the tube U. A is carried by the bearings

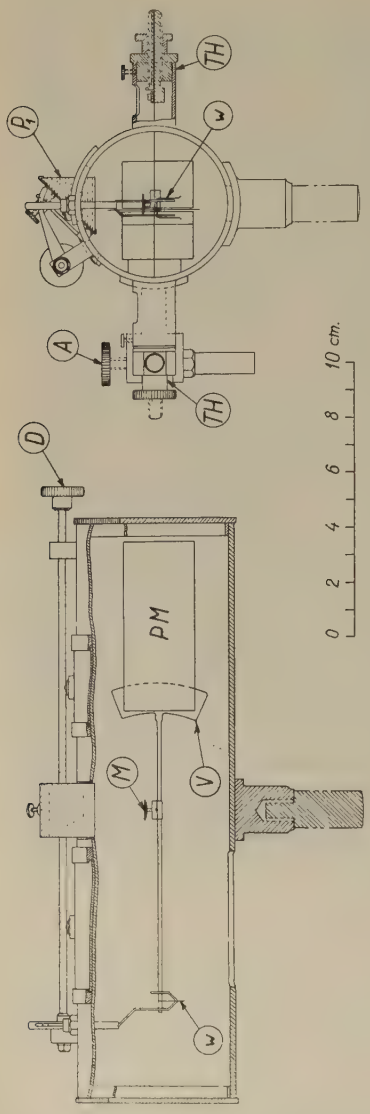

Fig. 5. Torsion balance.

B_1 and B_2, which are mounted at the ends of the tube U. Two horizontal slits D in the latter allow for the movement of the tube T in the horizontal plane. The tube U is mounted over a rectangular opening in the thermostat by means of the frame F. The bearing allows the polonium electrode to be moved to any part of the surface, while at the same time it is tight enough to permit the use of an inert gas atmosphere inside the thermostat box.

Balance.

Dervichian (l. c.) employs an ordinary type of balance with fairly long arms. In the first set-up we used an ordinary small analytical balance, but it was soon found that balances of this type have too high a moment of inertia to allow the glass slide to follow rapid variations in the surface pressure. This was especially evident in the study of the collapse of incompressible monolayers. A special torsion balance with a very light moving system was therefore constructed. The balance (Fig. 5 and T in Fig. 6) is mounted in a cylindrical house of brass which protects the moving system from draught. A thin beam of magnesium-aluminium alloy, having a cross-section of 2×1 mm, is fixed to the middle of a torsion wire (piano wire about 0.2 mm diam.). The wire is

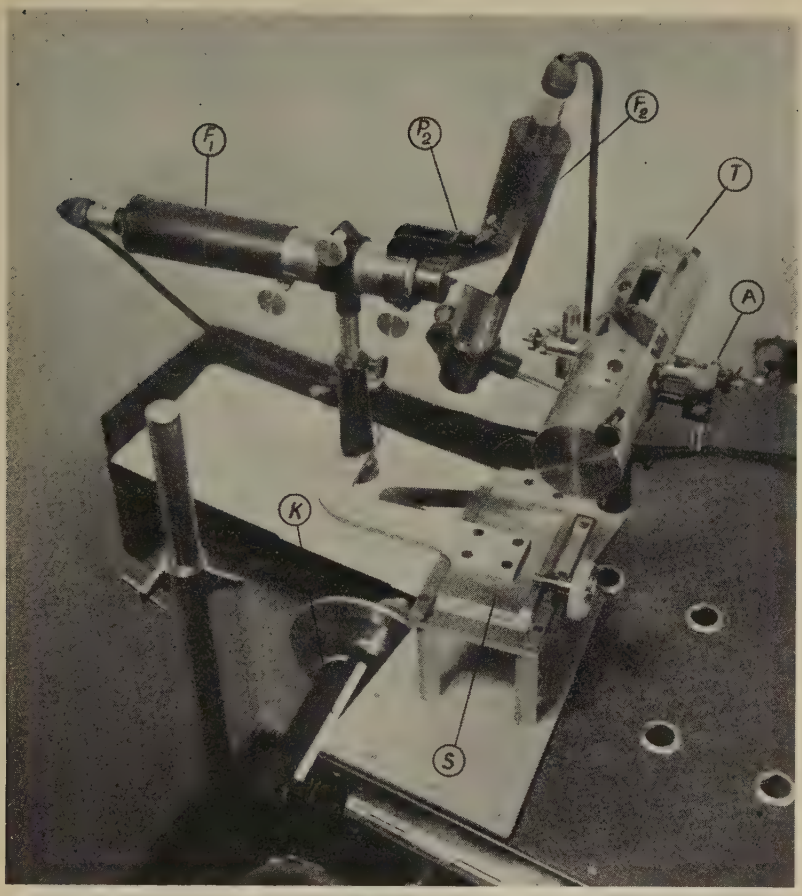

Fig. 6. Mounting of torsion balance and optical system. For explanation of letters see text.

stretched between two adjustable holders *TH* mounted in two tubes soldered on to the sides of the cylindrical house. Initial adjustment of the position of the balance beam is carried out by rotating one end of the torsion wire by means of a vernier *A*. The joint between beam and torsion wire has a small mirror *M*. The beam of light used for recording and the glass thread suspension for the glass slide pass through suitably placed openings in the house, which also has two openings on the top to provide access to the balance beam. The sensitivity of the balance may be altered in the ratios 1 : 2 : 3 by setting

the suspension of the slide at a distance of 2, 4 or 6 cm from the centre of rotation. Using glass slides of different perimeters a sensitivity variation of up to 1:10 may be obtained. If a greater range of sensitivities is wanted it is best to use two balances with different torsion wires. In order to provide an easy check on the sensitivity of the balance immediately before a run a rider *w* (usually 60 mg.) carried on the balance arm may be removed by a mechanical device (Fig. 5, *D*). Some form of damping for the moving system is usually necessary. The damping system employed by Dervichian, *i. e.* a horizontal metal plate suspended in a suitable liquid, may be used, but it increases the inertia of the moving system considerably. The damping system for the torsion balances used by us consists of an aluminium vane 0.3 mm thick, fixed to one end of the beam and moving in the air gap (1.2 mm wide) of a permanent magnet (Fig. 5, *V* and *PM*).

To maintain the position of the glass slide in the trough when the sensitivity is altered by setting the suspension at different positions along the balance beam, the balance and associated optical apparatus are mounted on an adjustable slide, the construction of which is shown in the photograph (Fig. 6, *S*). The lower part of the slide is securely fixed to the top of the thermostat.

Barrier and Camera Drive.

The successful operation of an automatic surface balance requires a very smoothly acting device for the continuous compression of the film and the synchronous movement of the photographic recording paper. After some trials with electric motors we decided to use the hydraulic drive mechanism[1] shown in Fig. 7. The outer cylinder is filled with oil (Shell transformer oil). At the beginning of the run the inner movable cylinder (piston) *P* is in the drawn-out position. The rate of fall of the piston is determined by the rate at which the oil enters the piston, and this is regulated by the adjustment of the conical valve *V* and by the total weight of the piston

[1] This device is similar to one used in a recording camera made by the *Cambridge Instrument Co., Ltd.*

and its associated weights *W* (2 kg. each). The valve-adjusting mechanism carries a scale which, after calibration, allows for any rate of fall between zero and 60 cm per min. When the piston is lifted the oil flows rapidly into the outer cylinder through the ball valve *B*. It is essential that no air be present in the outer cylinder, as this makes the piston fall in a jerky manner. Any air present may be allowed to escape by removing the screw *S* During a run a small amount of oil usually accumulates in the collar *C*. A small hole *H* allows this oil to flow into the piston when the latter reaches its lowest position. The piston may be fixed in any position by means of the clamping screw *CS*.

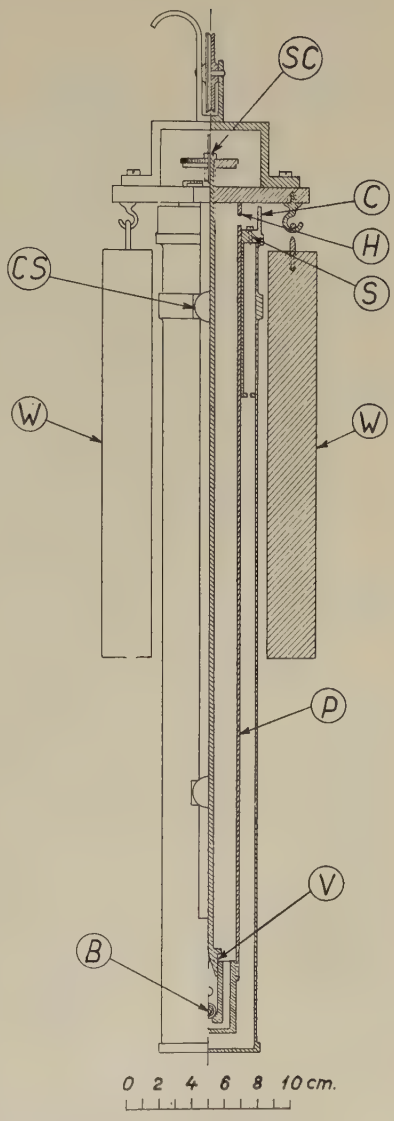

Fig. 7. Hydraulic drive mechanism.

The movement of the piston is transferred by means of a wire rope. One end of the wire is fixed, and it then passes in succession under the wheel at the top of the piston, over the wheel of the camera, under a small guide wheel, through the thermostat where the film compression device is attached, and finally on the other side of the thermostat over another guide wheel. The wire rope is kept taut by a weight of 1 kg. at the free end. The material of the wire is very important. It should be flexible, but must posses the smallest possible elasticity in the

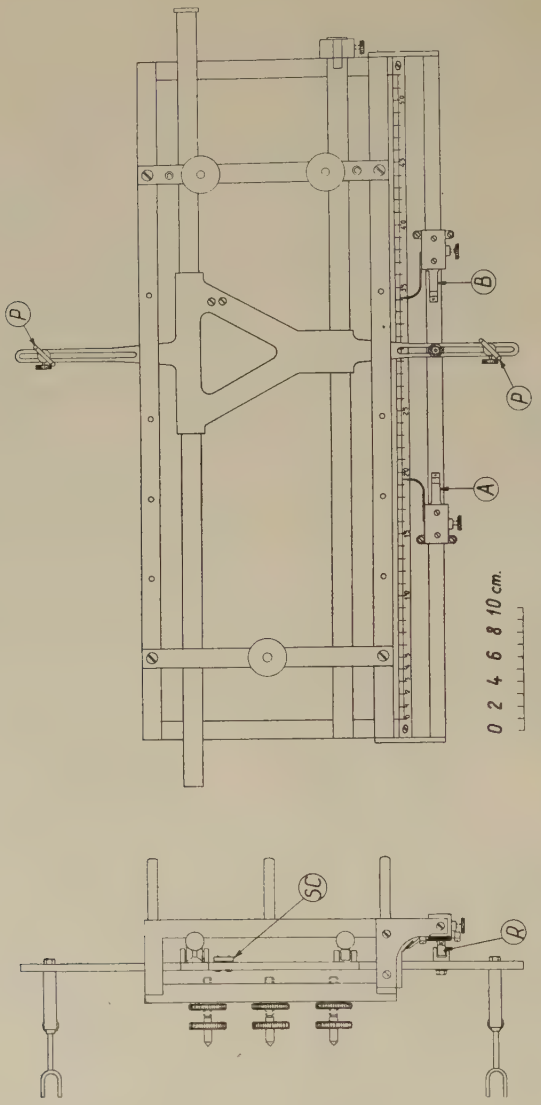

Fig. 8. Film compression device.

direction of the pull. Racket catgut was first used, but we now use a 49-stranded wire rope of stainless steel.[1] Seven parts of a wire rope made for surgical purposes, and consisting of seven wires each 0.05 mm in diameter, are combined

[1] Specially made by *Brukskoncernen*, Fagersta, Sweden.

to form a 49-stranded wire rope. This wire rope has proved very satisfactory.

The film compression device consists of a three-wheeled wagon (Fig. 8) which rolls on two chromium-plated brass rods. The two steering-wheels are shaped like cotton-reels, while the third rolling on the other brass rod has a plain cylindrical form. The wire rope is fixed to the underside of the wagon by means of a screw clamp (Fig. 8 *SC*). The position of the wagon may be read off on a millimeter scale. A signal lamp (Fig. 6 F_2) operated by two movable contacts (Fig. 8, *A* and *B* respectively) which are closed when a small contact wheel (Fig. 8 *R*) fixed to the wagon passes over them, marks the position of the wagon relative to the recorded force-area curve on the photographic paper.

The film is compressed by a glass barrier which glides along the edges of the trough. The barrier is moved by two adjustable forks (Fig. 8 *P*) fixed to the wagon.

The frame is supported by three legs which pass through holes in the bottom of the thermostat box and rest directly on the table.

Trough.

The troughs have the inside dimensions 15×52 cm, with a depth of 1.5 cm, and are made by sand-blasting from plate glass 2.5 cm thick. The long inside edges are made as sharp and parallel as possible. The rim has a width of 1 cm and is slightly ground in order to give a good grip for a paraffin coating. It would have been desirable to use hard glass, such as Pyrex, or still better fused quartz, as material for the trough, but we have been unable to obtain plates of sufficient thickness under present conditions.

Glass Slides.

The glass slides usually employed consist of standard microscope cover glasses $40 \times 25 \times 0.17$ mm. Two small holes each 2 mm in diameter are drilled near one of the short edges. The slide is hung vertically on a glass fork entering the holes. The glass fork is suspended from one arm of the balance by means of a glass thread 0.3—0.4 mm in diameter.

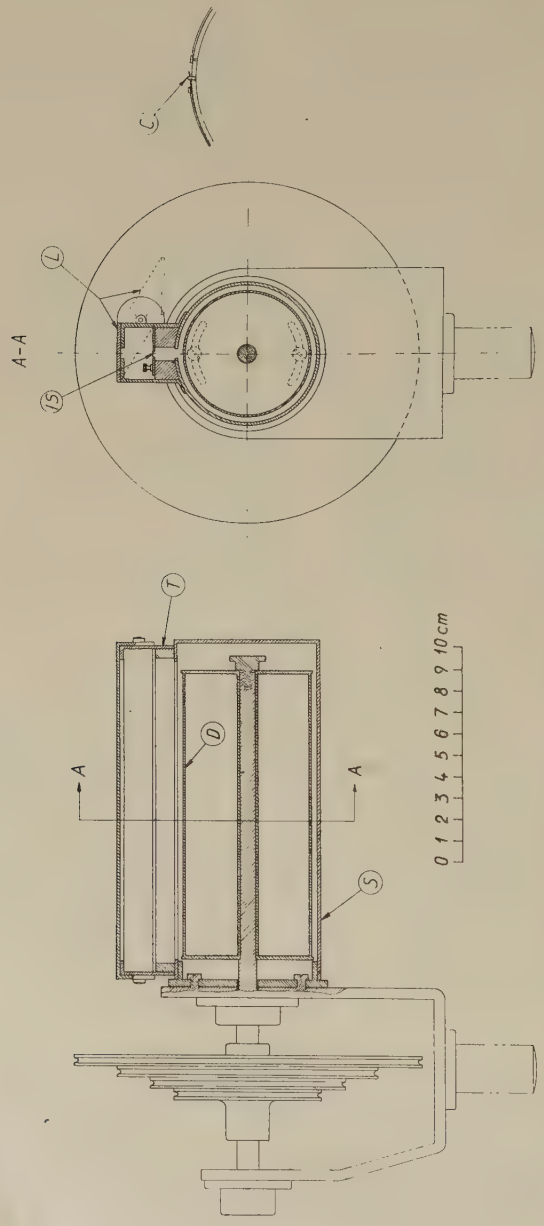

Fig. 9. Camera.

Camera.

The construction of the camera will be evident from Fig. 9. The removable light shield S is provided with a light trap T. The latter has a lid L, a wide outer slit and an inner slit IS, 0.2 mm wide. Recording papers 13×18 cm are used. The paper is kept in position by a transparent celluloid cover, which is fixed to the drum as shown in Fig. 9 C. The drum D has a diameter of 6 cm and may be driven by any of four wheels having diameters from 15.6 to 6.4 cm. The different wheels allow different ratios between the movements of the barrier and the recording paper to be used.

The optical system is as follows (cf. Figs. 1 and 6). The light from a straight filament lamp F_1 is reflected by the prism P_1 on to the mirror of the balance and further by the prisms P_1 and P_2 on to the slit of the camera K, and is brought to focus on the recording paper by means of a well-corrected lens L inserted between the lamp and the prism P_1. In order to allow the beam of light to fall perpendicularly on to the middle of the recording paper, the long axes of the camera and balance beam are set at an angle of about 75° to the movement of the wagon. In order to avoid over- or under-exposure of the photographic paper the current through the lamp F_1 must be adjusted to the speed of compression used. For this purpose a rheostat and an ammeter (see Fig. 2) are inserted in series with the filament.

The apparatus is of course sensitive to vibration and is therefore mounted on a very stout table constructed of steel tubes and with a top of stone 2.5 cm thick. The legs of the table rest on plates of cork.

Experimental Procedure.

Preparation of Trough, Barriers and Glass Slides.

Old paraffin coating is removed from the edges of the trough by means of a suitable solvent and cotton-wool. The trough, with the serpentine tube inserted, is filled with chromic acid-sulphuric acid mixture, which is allowed to flow over the rim.

The tube and the trough are carefully washed with distilled water and dried, avoiding dust. The rim of the trough is given a light coating of paraffin wax. The latter should be tested for spreading impurities (*Merck*, "reizungslos für Tierversuche", or *British Drug Houses*, "Paraffin Wax, congealing point about 60°", are usually suitable). It is convenient to use a solution of paraffin wax in light petroleum (b. p. 60—80°) which is applied to the rim of the trough by means of a brush (made from a glass rod and cotton gauze) carried in the stopper of the bottle. The paraffin coating should be applied to the upper surface of the edges only, and paraffin wax on the inside edges should be carefully removed. Both the solvent used for the paraffin solution and the solvent in which the film-forming substance is to be dissolved should be distilled in an all-glass apparatus before use. The barriers used for cleaning the surface and for compressing the film consist of glass strips having the dimensions $250 \times 10 \times 2$ mm. They are carefully cleaned and given a light coating of paraffin wax. The glass slide with its attached hook is kept in chromic acid-sulphuric acid mixture and carefully rinsed with distilled water immediately before use. Ordinary laboratory distilled water may contain surface active impurities. Conductivity water should preferably be employed, and may be conveniently obtained by a still of the type described by Ellis and Kiehl (5). When working with a vertical type of surface balance a very high degree of cleanliness is essential, as this type of balance does not allow the cleaning of the surface to be checked as easily as does the horizontal type.

Adjusting the Apparatus for a Run.

The trough is inserted in its position in the thermostat as shown in Fig. 3. One of the adjusting screws rests in a hole and another in a V-shaped groove in two small metal plates fixed underneath the trough. The long edges of the trough should be parallel to the wire rope. The serpentine glass tube is connected to the thermostat system and the latter adjusted to the desired temperature. The trough is filled to the rim with substrate, and adjusted in the horizontal position by means of the three screws.

The camera is loaded, and a suitable relation between barrier and camera movement chosen. The valve of the piston is adjusted for the desired rate of compression, and the sensitivity of the balance given a suitable value.

The electric contacts (A and B in Fig. 8) are now adjusted. If these are to mark the areas A and B sq. Å. per molecule respectively and the contact A is placed at a cm from the end of the trough, the other contact B is of course placed at $\frac{B}{A} \times a$ cm from the end. Let us now assume that a substance of mol. weight W is to be spread from a solution containing n mg. of substance per ml. If N_0 represents AVOGADRO's number[1] and the width of the trough is p cm, the amount of solution to be taken (x ml.) may be calculated as follows. The number of molecules contained in x ml. is $\frac{x \cdot n \cdot N_0}{W \cdot 10^3}$. When the barrier is in a position at a cm from the end of the trough, these molecules are distributed over an area of $a \cdot p \cdot 10^{16}$ sq. Å. The area per molecule is thus

$$A = \frac{W \cdot 10^3 \cdot a \cdot p \cdot 10^{16}}{x \cdot n \cdot N_0} \text{ sq. Å}$$

which gives

$$x = \frac{a \cdot p \cdot W \cdot 10^{19}}{n \cdot N_0 \cdot A} \text{ ml.}$$

The concentration of the solution to be spread should be chosen to give a value for x of 0.1—0.2 ml.

The surface of the substrate is now cleaned by sweeping it several times in succession with glass barriers. The surface contamination collected by the barriers is carefully removed by suction. The glass barrier used for compression is then put in position between the prongs of the forks.

The glass slide is hung in and adjusted in the vertical position. The lid is closed, and one now waits for a short time (two to five minutes) in order to allow excess water to drain off from the slide, and temperature and moisture equilibrium to be attained. The zero point of the balance is then adjusted

[1] The revised value for AVOGADRO's number given recently by BIRGE (6) is $N_0 = (6.0228_8 \pm 0.0011)\, 10^{23}$ mole^{-1}.

and the sensitivity tested. For this purpose the rider is removed from the balance beam, the piston released and the barrier allowed to move forward a short distance with the lid of the light trap open. Repetition of this procedure with the rider in position gives the zero line. Through the small door in the lid the calculated amount of the spreading solution is now put on to the surface by means of an "Agla" micrometer syringe.[1] Care is taken to see that the drops of the solution are not all allowed to fall on the same point of the surface. After spreading, a short time (one to ten minutes, depending on the solvent used and the substance being spread) is allowed to elapse so that the solvent may evaporate and the molecules spread out properly over the surface. The piston is then released and the force-area curve recorded.

Estimated Accuracy of Force-Area Measurements.

In the *pressure measurements* three types of error may be distinguished. The first of these is due to uncertainty in the determination of the different parameters of eq. (8). The ratio between the balance arms l_1 and l_2, as well as the true weight of the calibration weight w, may be determined with a high degree of accuracy. The perimeter of the glass slide and the recorded readings s_f and s_w are all of the order of 50 mm, and may be measured within $\pm$ 0.1 mm or $\pm$ 0.2 per cent. The average error due to the parameters of eq. (8) should therefore be less than $\pm$ 0.4 per cent. The second type of error is due to mechanical causes such as hysteresis in the torsion wire, or change in the height of the mid-point of the wire with varying load. From a series of calibration experiments it appears that the mechanical errors are less than $\pm$ 0.2 per cent.

Finally, we have errors involved in the recording. The maximum value of $\theta_0 - \theta_f = \Delta\theta$ (cf. Fig. 1) is in the present case 6°. With the arrangement used, the balance beam is in the horizontal position and the beam of light is perpendicular to the axis of the camera at 50 per cent of full deflexion. If

[1] This instrument is obtainable from Messrs. *Burroughs Wellcome & Co., Ltd.*, London, England.

the point at 40 per cent of full scale deflexion is calibrated by means of the weight w, the recording error over the range 25 to 100 per cent of full scale deflexion will be less than ± 0.2 per cent. Below 25 per cent deflexion the error increases to about $+0.5$ per cent at very small deflexions. Large accidental errors may occur if the contact angle differs from zero. As the slide moves continually upwards it is possible, however, to maintain a contact angle of zero even for solid monolayers. Harkins and Anderson (7) have shown that the Wilhelmy method gives results identical with the Langmuir-Adam method even for very solid monolayers, *e. g.* for calcium stearate. When condensed (mesomorphous or solid) monolayers that may form multilayers on glass are investigated, care must be taken to prevent water ripples or oscillations of the balance to cause deposition of a multilayer on the slide. The latter is then no longer wetted properly and the contact angle is not zero.

The error in the *area measurements* arising from want of parallelism and linearity of the inside edges of the troughs used is less than ± 0.15 per cent. The solutions used for spreading can be made up with a high degree of accuracy. The "Agla" micrometer syringes deliver volumes of the order of 0.1 ml to within ± 0.2 per cent. The errors mentioned, together with errors due to uncertainty in the position of the barrier and the signals, give an estimated average error of ± 0.4 per cent.

Large accidental errors may arise from faulty spreading technique. If the drops of the spreading solution are put on to the surface too rapidly the solvent may flow out and dissolve paraffin wax from the edges of the trough. If the compression is started before the molecules have spread properly small areas will result. Errors due to this cause are, of course, most frequent with solid monolayers. As an example of the reproducibility of the spreading process we may take a series of eight successive runs with liquid condensed monolayers of ethyl α-bromobehenate at 20° C. The largest deviation from the mean area at two dynes pressure was 0.44 per cent. For monolayers which can be deposited on glass an error may be caused in the area measurements by the deposition of a monolayer on the rising slide. The magnitude of this error may

of course be calculated, and when present it usually does not exceed 0.5 per cent with the apparatus described.

In careful work under normal conditions the accuracy obtained both in pressure and area measurements is thus well within one per cent.

At the extreme ends of the temperature range the accuracy of both pressure and area measurements is, of course, less than in the middle region. A source of error in the pressure measurements at temperatures much above or below room temperature is condensation of water on the suspension of the glass slide at the point where it passes through the hole in the thermostat.

Examples of the Use of the Balance.

Fig. 10 shows the automatically recorded force-area curve for a very pure specimen of stearic acid[1] spread on acid substrate at 20.0°. In the lower compressible region the force-

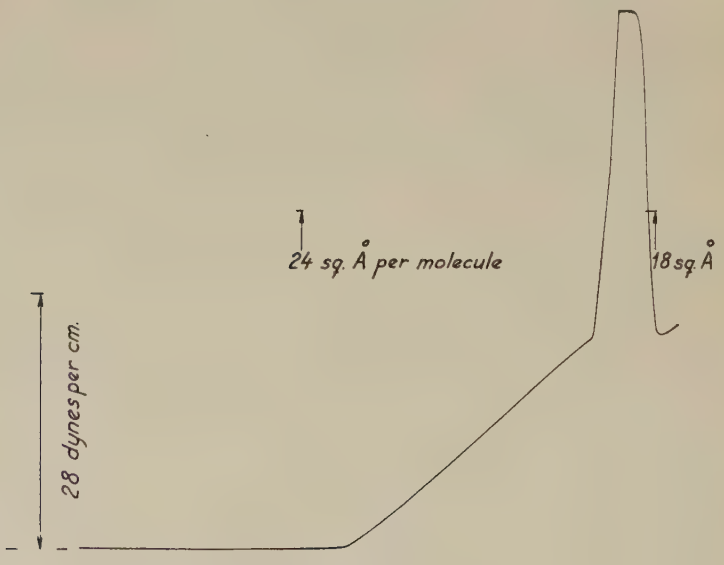

Fig. 10. Force-area curve for stearic acid spread on 0.01 N hydrochloric acid at 20° C. Rate of compression 6 cm per minute.

[1] The specimen used had a setting point of 69.40° ± 0.02° C and was obtained from Professor F. Francis, Bristol, England.

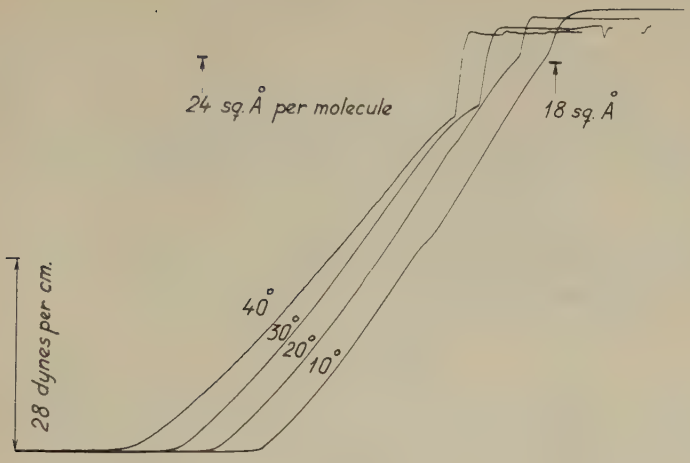

Fig. 11. Force-area curves for 1,2-dihydroxyheneicosane at 10°, 20°, 30° and 40° C respectively. Substrate: 0.01 N hydrochloric acid.

area curve is approximately linear. The high-pressure region consists of two parts, and there is a change to a steeper slope at about 40 dynes. NUTTING and HARKINS (8), using the ordinary LANGMUIR-ADAM balance and stepwise compression, obtained similar curves for normal chain primary alcohols but were unable to obtain the upper part of the high pressure region for the corresponding carboxylic acids, as the monolayers were too unstable. DERVICHIAN (2) has published an automatically recorded force-area curve for stearic acid on acid (0.002 N hydrochloric acid) substrate. His force-area curve shows no distinct change of slope of the high pressure region, and the collapse at 61 dynes pressure has the form of a fairly sharp peak. In our curve (Fig. 10) the pressure remains at 60 dynes for a while after the collapse has set in. These differences may be due to different purity of the stearic acid specimens used, but it is more probable that the comparatively high moment of inertia of the balance used by DERVICHIAN prevented it from following the very rapid variations involved.

Fig. 11 shows the force-area curves of 1,2-dihydroxyheneicosane[1], for four different temperatures. The curves are recorded in succession on the same paper. The curves for 10°

[1] The synthesis of this glycol will be described elsewhere by one of us (S. S.).

and 20° show a slight kink at about 30 and 40 dynes pressure respectively. It is possible that both this feature and the transition to an incompressible region above 60 dynes pressure would have been missed if the compression had been carried out stepwise with a horizontal type of balance. The curve for 40° shows small irregularities. These are due to the difficulty of avoiding small ripples on the water surface at this high temperature. The viscosity of water at 40° is only about half that at 10°.

Acknowledgements.

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Summary.

The design and use of a thermostated automatically recording surface balance of the Wilhelmy-Dervichian type for work in the temperature range 0° to +55° C is described. Special features of the instrument are a torsion balance with a very low moment of inertia and a very smoothly acting hydraulic drive mechanism which allows a continuous range of compression rates to be used. The accuracy of the balance is discussed, and some examples of its use are given.

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Über lichtelektrische Extinktionsmessungen mit Hilfe von Multiplikatorzellen.

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Vor einigen Jahren wurde im hiesigen Institut mit Hilfe von Selensperrschichtzellen ein lichtelektrisches Photometer gebaut (Bodforss (1)), das seitdem sehr gut funktioniert und trotz seiner ziemlich primitiven Bauweise bei mehreren Untersuchungen gute Dienste geleistet hat (Bodforss und Leden (2), Holst (3), Adell (4)).

Nun ist die Verwendung von Selenzellen für genaue Messungen nicht ohne weiteres statthaft. (Vgl. z. B. Björnståhl (5).) So ist wohlbekannt, dass der Photostrom nicht proportional der Belichtung anwächst. Die Strom-Lichtstärkekurve ist für ein gegebenes Photoelement vom Widerstand des Messkreises abhängig. In extremen Fällen kann auch die Wellenlänge des Lichtes von Bedeutung sein. Wir haben eine Selenzelle gehabt, die bei Belichtung mit unzerlegtem Glühlampenlicht „normal" funktionierte aber bei Abfiltrierung des kurzwelligen Lichtes verhältnismässig immer unempfindlicher wurde, um in dunklem Rot ihre Stromrichtung zu wechseln. Die Erklärung ist wahrscheinlich einfach. Das Selen hat im sichtbaren (und wahrscheinlich auch im ultravioletten) Spektrum eine hohe Extinktion. Die Selensperrschichtzellen können deshalb in diesem Spektralgebiet nur als Vorderwandzellen wirken, ein Effekt, der im Gelbgrün ein scharfes Maximum besitzt. Für langwelliges Licht ist die Sperrschicht aber durchlässig. Es tritt dabei ein Hinterwandeffekt auf, wodurch der Vorderwandeffekt aufgehoben oder sogar überkompensiert werden kann.

Die Zweckmässigkeit und genügende Genauigkeit des in (1) beschriebenen Instrumentes wurde empirisch geprüft. Eine derartige Prüfung ist, wie unten gezeigt wird, gar nicht so einfach. Es wurden folgende Methoden herangezogen.

1. Der gefundene molare Extinktionskoeffizient ε von Kaliumpermanganat zeigte sich in einer Verdünnungsserie genügend konstant. Da das Beersche Gesetz bei den verwendeten hohen Verdünnungen aller Wahrscheinlichkeit nach (Vgl. Kortüm (6)) streng gültig ist, dürfte die Bestimmung des molaren Extinktionskoeffizienten von Kaliumpermanganat prinzipiell sehr zweckmässig als Prüfungsmethode sein, fordert aber wegen der Zersetzlichkeit der Lösungen eine sehr rasche und saubere Arbeit. Hochmolekulare organische Farbstoffe sind zu vermeiden, da sie oft irreversibel an die Küvettenwände adsorbiert werden. Das von v. Halban und Wieland (7) als optische Standardsubstanz empfohlene Astraphloxinperchlorat ist gewiss mit Vorsicht zu benutzen.

2. Durch Bestimmung des Abstandquadrates konnte für die fraglichen Zellen und die gegebene Belichtung bei dem verwendeten äusseren Widerstand (26 Ohm) innerhalb 1 bis 2 % Proportionalität zwischen Belichtung und Photostrom nachgewiesen werden. Die Lichtquelle war eine Mikroglühlampe, der Photostrom (minimal) $4 \cdot 10^{-7}$ Amp. Die Entfernungen wurden zwischen 25 und 250 cm variiert. Wie die Messungen von Björnståhl (5) gezeigt haben, ist solch eine Genauigkeit für jede beliebige Zelle und Zellenschaltung nicht zu erwarten.

3. Bei Messung der Abbleichungsgeschwindigkeit von Phenolphtalein in starker Natronlauge, einer Reaktion, die pseudomonomolekular erfolgt, wurden so gute Geschwindigkeitskonstanten gefunden (1, 2), dass es berechtigt erscheint, rückwärts auf genügende Proportionalität zwischen Photostrom und Lichtstärke zu schliessen. Die Schwankungen der Messwerte kamen dadurch zustande, dass die Lichtquelle (eine Quecksilberlampe nach v. Hippel) in Ermanglung einer Akkumulatorbatterie an die Lichtleitung angeschlossen war.

Wegen ihrer einfachen Bedienung und ihrer Stabilität sind solche mit Kompensationsschaltung arbeitende Sperrschichtzellen sehr zu empfehlen; sie müssen aber durch irgend eine genügend einwandfreie Methode etwa wie oben geprüft werden.

Diese Kontrolle muss auch ab und zu wiederholt werden, da die Selenelemente ihre Eigenschaften mit der Zeit ändern.

Um die Genauigkeit der Messungen etwas weiter treiben zu können, haben wir ein neues Instrument mit Alkaliphotozellen gebaut. Bei den gewöhnlichen Zellen (wenigstens bei denjenigen, die uns unter den jetzigen Verhältnissen zur Verfügung standen) können aber Galvanometer mittlerer Empfindlichkeit kaum benutzt werden. Elektrometer sind bei Routinearbeit am liebsten zu vermeiden. Wir haben deshalb die neuen Photozellen mit Sekundäremission geprüft.

Zur Verwendung kamen zwei Philips' Zellen 3 520, die in Kompensationsschaltung arbeiteten (Fig. 1). Die Zellen waren cäsiumbelegte Hochvakuumröhren, die beide für eine Betriebsanodenspannung von 635 Volt gebaut waren. Die übrigen Betriebsdaten waren auch möglichst gleich. Die Empfindlichkeit ist angeblich ca 2 000 μA/Lm, also etwa 100-mal grösser als die einer ähnlichen Zelle ohne Sekundäremission. Es ist dadurch möglich, die Messungen mit einem gewöhnlichen hochohmigen Galvanometer (Empfindlichkeit 10^{-9} Amp/Skalenteil) auszuführen.

In Fig. 2 ist eine Photozelle mit angeschlossenem Spannungsteiler gezeichnet. Die Hochohmwiderstände KA_1, A_1KS_1 u. s. w. sind so berechnet, dass die Elektroden die vom Fabrikanten vorgeschriebenen Spannungen bekommen. Da die Röhren nicht ganz gleich sind, musste für jede ein solcher Spannungsteiler angefertigt werden.

Nun kann man natürlich in Prinzip einfach die Spannungen einer für beide Zellen gemeinsamen, in Stufen unterteilten Trockenbatterie entnehmen. Aber, abgesehen von der schlechten Beschaffenheit der jetzigen Batterien, die eine tägliche Nachprüfung der Spannungen erfordern, entstehen durch die zahlreichen, einander überquerenden Drahtverbindungen Isolationsschwierigkeiten.

Die Betriebsspannung 635 V muss möglichst konstant sein. Um die Trockenbatterien wenigstens teilweise los zu werden, wurde mit gutem Erfolg der in Fig. 3 skizzierte stabilisierte Gleichstromsgenerator verwendet. Wechselstrom des Institutnetzes (220 V), stabilisiert durch einen automatischen Brown-Boveri-Regulator, wurde auf 2×700 V transformiert und mit

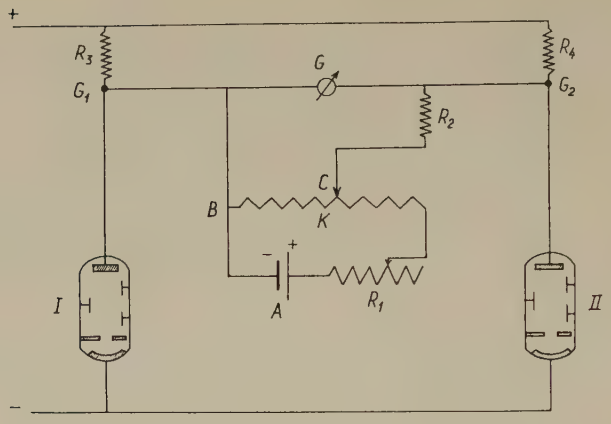

Fig. 1. Kompensationsschaltung.

I und II Multiplikatorzellen; A Akkumulator; K Drahtmessbrücke bzw. Potentiometer; B Nullende von K; C Läufer; G Galvanometer; R_1 Kurbelrheostat; $R_2 = R_3 = R_4 = 5 \cdot 10^5$ Ohm.

Hilfe der Gleichrichterröhre *AZ1* und des Kondensators C_1 (2 μF) gleichgerichtet. Die Röhre *6J7* ist eine Pentode, die durch den Glühstrom *a—b* geheitzt wird. Werden die Steuergitter durch zwei genügend konstante Trockenbatterien B_1 und B_2 aufgeladen, erreicht man, dass die Ausgangsspannung konstant bleibt, obgleich die Eingangsspannung fluktuiert. Nähere Angaben über dieses Regelprinzip sind von Lindenhovius und Rinia (8) gemacht worden. Das Gerät funktioniert sehr gut und zeigt eine hohe Spannungskonstanz. Es ist den gewöhn-

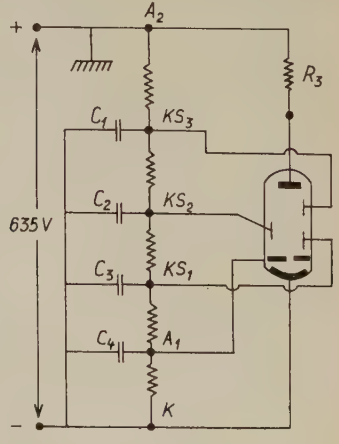

Fig. 2. Multiplikatorphotozelle mit Spannungsteiler.

K mit der lichtempfindlichen Kathode, A_1 mit der ersten Anode, KS_1, KS_2 und KS_3 mit den sekundär emittierenden Hilfselektroden, A_2 mit der Endanode verbunden.
C_1—C_4 Kondensatoren (0.1 μF)
$R_3 = 500\,000$ Ohm.

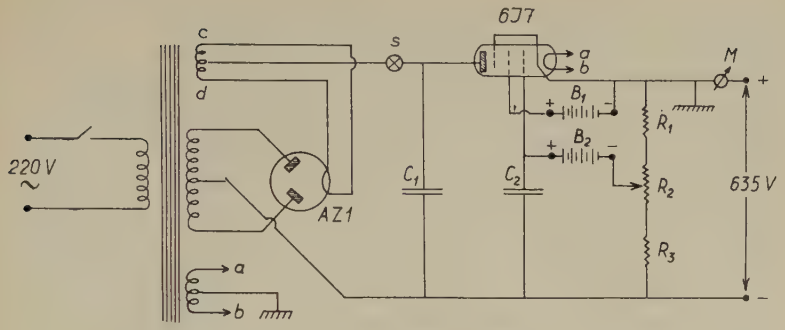

Fig. 3. Spannungsstabilisator.

AZ1 Ventilrohr, *a*—*b* Glühstromtransformator (2 × 3,15 V); *c*—*d* Glühstrom (2 × 4 V); *S.* Sicherung; *6J7* Pentode; C_1 und C_2 Kondensatoren (2 µF); R_2 Potentiometer (100 kΩ); $R_1 = 100$ kΩ; $R_3 = 1$ MΩ; B_1 und B_2 Trockenbatterien, je etwa 50 V. Die gewünschte Spannung 635 V wird erhalten, wenn R_2 so eingestellt wird, dass 1 Milliampere, gemessen an *M*, durch die angeschlossenen Spannungsteiler (Fig. 2) fliesst.

lichen Neonstabilisatoren weit überlegen. Diese waren in unsrem Falle nicht zu gebrauchen, da sie (Philips' Neonröhre 150 A) die momentanen Störungen in der Netzspannung nicht zu unterdrücken vermochten.

Die *Kompensationsschaltung* geht aus Fig. 1 hervor: Sie besteht aus einer Drahtmessbrücke oder Potentiometer *K*, das mit dem Akkumulator *A* über den Kurbelrheostaten R_1 gespeist wird. R_2 ist ein Widerstand von 500 000 Ohm. Werden beide Zellen durch dieselbe Lichtquelle beleuchtet, entsteht, wenn die Zellen und die Lichtströme nicht ganz gleich sind, zwischen G_1 und G_2 eine Spannungsdifferenz *P*, die mit Hilfe von *K* kompensiert werden kann.

P sei z. B. positiv und der Akkumulator folglich wie in Fig. 1 eingeschaltet. Um das Galvanometer auf Null zu bringen, seien *a* Tausendstel des ganzen Brückendrahtes zwischen *B* und *C* erforderlich. Es gilt dann

$$P = E \cdot r_g \cdot k \frac{a}{(R_2 + r_g + k\,a)\,(R_1 + 1\,000\,k) - k^2\,a^2}$$

E ist hier die E. M. K. des Akkumulators, r_g und $k\,a$ der Widerstand des Galvanometers bzw. des Messdrahtes zwischen *B* und *C*. Da $R_1 \simeq 70$ Ohm, $R_2 = 500\,000$ Ohm, $r_g = 1\,000$ Ohm, $1\,000\,k = 26$ Ohm ist, kann $k\,a$ bzw. $k^2\,a^2$ im Nenner des Aus-

druckes ganz vernachlässigt werden, und bei festgelegtem R_1 wird P der Brückenablesung a proportional.

Die Messung der Extinktion einer Versuchslösung für monochromatisches Licht soll demnach auf folgende Weise ausgeführt werden. (Über die Monochromatisierung siehe unten!)

1. Man bringt den Läufer C der Messbrücke K auf 0, d. h. die Kompensationsapparatur AR_1K wird ganz ausgeschaltet. Beide Zellen werden mit schwach konvergentem Licht aus der Quecksilberlampe voll beleuchtet (Bodforss (1)), und in den Strahlengang einer der Zellen, der „Versuchszelle" I, führt man die mit Wasser gefüllte Küvette ein. Mit Hilfe von Irisblenden wird die Beleuchtung jeder Zelle dann so reguliert, dass das Galvanometer G keinen Ausschlag gibt.

2. Im zweiten Moment führt man den Läufer zum anderen Ende der Brücke über (= stellt ihn auf 1 000 Skalenteile ein), und die Versuchszelle wird ganz verdunkelt, oder was damit gleichbedeutend ist, die Extinktion der Versuchslösung wird unendlich gross gemacht. Durch Variation des Widerstandes in R_1 wird das Galvanometer dann wieder stromlos gemacht.

3. Schliesslich wird die Küvette mit der Versuchslösung gefüllt, und mit den Blenden und dem Rheostaten R_1 in unveränderter Lage verschiebt man den Läufer, bis nochmals kein Strom durch das Galvanometer geht. BC umfasse dann a Tausendstel des Messdrahtes.

Die Zellen I und II werden von Licht der Intensitäten I_{I} und I_{II} getroffen, und es werde angenommen, dass die entsprechenden Sekundäremissionsströme i_{I} und i_{II} den Lichtintensitäten proportional seien. Dann gilt ganz allgemein

$$P = F \cdot a = f_1 \cdot (i_{\mathrm{II}} - i_{\mathrm{I}}) = f_2 \cdot I_{\mathrm{II}} - f_3 \cdot I_{\mathrm{I}}$$

(F, f_1, f_2 und f_3 sind Proportionalitätsfaktoren).

Im ersten Moment der Messung hat man $i_{\mathrm{I}} = i_{\mathrm{II}} = i_0$. Die i_{I} und i_{II} entsprechenden Lichtintensitäten seien I_0 und I_{II} geschrieben.

Dann gilt

$$F \cdot 0 = f_1 (i_0 - i_0) = f_2 \ I_{\mathrm{II}} - f_3 \cdot I_0.$$

Im zweiten Moment wird $i_{\mathrm{I}} = 0$ und i_{II} unverändert gleich i_0. Die Gleichung wird also:

$$F \cdot 1\,000 = f_1 \cdot (i_0 - 0) = f_2 \cdot I_{\mathrm{II}}.$$

Im dritten Messungsmoment hat man

$$i_{\mathrm{I}} = i_D,\ i_{\mathrm{II}} = i_0,\ I_{\mathrm{I}} = I_D;\ I_{\mathrm{II}} = I_{\mathrm{II}}$$

und damit

$$P = F \cdot a = f_1 (i_0 - i_D) = f_2 \cdot I_{\mathrm{II}} - f_3 \cdot I_D.$$

I_0 und I_D sind also die Intensitäten des Lichtes, das dieselbe Küvette mit Wasser, bzw. mit Versuchslösung gefüllt, passiert hat.

Eine Kombination der drei Gleichungen gibt:

$$\frac{a}{1\,000} = \frac{I_0 - I_D}{I_0}$$

oder nach einfachen Umformungen für die Extinktion E der Versuchslösung:

$$E = \log \frac{1\,000}{1\,000 - a}.$$

Prüfung. Es ist anzunehmen, dass in den vorliegenden Röhren, die ja Hochvakuumröhren sind, der Primärphotostrom mit genügender Genauigkeit der Belichtung proportional ist (Larson und Salinger (9); Winans und Pierce (10)). Da die Sekundärphotokathoden zum Teil von Licht getroffen werden, ist doch eine genauere Prüfung des Sekundäremissionsstroms wünschenswert. Eine derartige Prüfung ist ohne sehr grosse Mittel nicht leicht. Ein erster Versuch wurde durch Variation der Schichtdicke einer lichtabsorbierenden Lösung mit Hilfe einer Präzisionsschraubenküvette von Hilger gemacht. Die Methode zeigte sich aber nicht genügend genau, wahrscheinlich weil eine Veränderung der Schichtdicke (obgleich maximal nur 5 mm) eine kleine Änderung im geometrischen Strahlengang hervorrief. Das mag als eine Warnung für die Verwendung von Baily-röhren bei genaueren Messungen dienen.

Die endgültigen Versuche wurden mit einem rotierenden Sektor gemacht, der auch während der Rotation eingestellt und abgelesen werden konnte (Olerup (11)). Da wir bei unseren Versuchen von einer genügend stabilen Montierung absehen mussten, sind die Messungen wahrscheinlich durch gewisse Erschütterungseffekte gestört.

Als Lichtquelle diente bei diesen Versuchen eine Mikroglühlampe, wie sie zu gewissen medizinischen Zwecken verwendet wird. Sie war in einem geschwärzten Gehäuse montiert und brannte im Fokus eines photographischen Objektives. Falsches Licht, das durch Reflexionseffekte reichlich auftritt, wurde so weit möglich abgeblendet. Die Lampe wurde zuerst über Vorschaltwiderstände der grossen 12-Voltbatterie des Instituts angeschlossen. Trotzdem zeigte der Photostrom sehr störende, momentane Schwankungen auf, die eine Inkonstanz der Lampe anzeigten.

Es erwies sich zuletzt, dass diese Störungen aus dem Wechselstromnetz stammten und durch Induktion oder unentdeckbare Isolationsfehler auf die Akkumulatorleitungen übergeführt wurden. Es blieb dann nichts anders übrig, als die Lampe mit dicht nebenan aufgestellten tragbaren Akkumulatoren zu speichern.

Wenn der Sektor eingeschaltet wird, tritt ein starker Wind auf, der trotz guter Isolation mit wollenen Tüchern die Lampenspannung merkbar beeinflusst. Der Sektor muss demnach während der ganzen Messung mit konstanter Geschwindigkeit rotieren (Gleichstrommotor, an eine 240-Volt Batterie angeschlossen).

Bei diesen Prüfungen wurde eine der Multiplikatorzellen ausgeschaltet und die Kompensationsanordnung mit den Endelektroden der anderen verbunden.

Falls der Öffnungswinkel der beiden diametral angebrachten Ausschnitte des Sektors in zwei Fällen mit v_1 und v_2 bezeichnet wird und wenn die Intensität des durchgelassenen Lichtes entsprechend $(I_D)_1$ und $(I_D)_2$ geschrieben wird, so hat man für die relative Extinktion E_2 im zweiten Falle:

$$E_2 = \log \frac{(I_D)_1}{(I_D)_2} = \log \frac{v_1}{v_2}.$$

Anderseits kann E_2 analog mit den Berechnungen auf S. 38—39 aus den Brückenablesungen, also aus der Stärke des Emissionsstromes, ermittelt werden. Tabelle 1 gibt die Resultate von drei Versuchsreihen dieser Art wieder. Alle diese relativen Extinktionswerte sind auf $v_1 = 89°,72$ als Bezugswinkel zurückgeführt. Die gute Übereinstimmung der Brückenwerte mit dem

Tabelle 1. Vergleich von relativen Extinktionswerten, einerseits aus Sektorwinkeln, anderseits aus Brückenablesungen errechnet.

Sektorwinkel	Relative Extinktion berechnet aus				Abweichung des Brückenwertes vom Winkelwert in %		
	den Winkeln	den Brückenablesungen					
		I	II	III	I	II	III
89°,72	0,0000	0,0000	0,0000	0,0000	—	—	—
80°,71	0,04596	0,04543	0,04576	0,04564	−1,2	−0,4	−0,7
71°,71	0,09731	0,09708	0,09742	0,09739	−0,2	−0,1	−0,1
62°,74	0,1554	0,1555	0,1553	0,1558	+0,1	−0,1	+0,3
53°,75	0,2225	0,2229	0,2226	0,2235	+0,2	0,0	+0,4
44°,72	0,3024	0,3034	0,3031	0,3036	+0,3	+0,2	+0,4
35,°75	0,3996	0,4018	0,4003	0,4014	+0,4	+0,2	+0,4
26°,72	0,5261	0,5283	0,5265	0,5289	+0,4	+0,1	+0,5
17°,71	0,7045	0,7083	0,7043	0,7086	+0,5	0,0	+0,6
8°,72	1,012	1,017	1,010	1,017	+0,5	−0,2	+0,5
6°,92	1,118	1,118	1,111	1,121	+0,4	−0,2	+0,7
5°,12	1,244	1,250	1,240	1,251	+0,5	−0,3	+0,6
3°,30	1,434	1,447	1,429	1,444	+0,9	−0,3	+0,7
1°,52	1,771	1,773	1,752	1,789	+0,1	−1,1	+1,0

zugehörigen Winkelwert spricht stark für die Annahme, dass der Sekundäremissionsstrom proportional der Lichtintensität sei.

Wie v. Halban, Olerup und andere gezeigt haben, lassen sich absolute Extinktionsmessungen nur mit einer bescheidenen Genauigkeit von 1—2 % ausführen. Dies hängt wahrscheinlich besonders mit Reflexionseffekten an den Küvettenwänden zusammen. Unter solchen Umständen ist die von uns gefundene Genauigkeit mehr als genügend.

Mit Hilfe von zwei Multiplikatorzellen wurde weiter die Extinktion einer Standardlösung von der Zusammensetzung $7{,}5 \cdot 10^{-5}$ mol. Pikrinsäure + 0,005 mol. Natriumhydroxid nach der oben (S. 38—39) angegebenen Methode bestimmt. Bei einer Schichtdicke von 2,6 cm und für Licht von der Wellenlänge 436 mμ wurde bei 20°,0 C der Wert 0,8182 erhalten. Das gibt für den molekularen Extinktionskoeffizienten ε den Wert 4 196

oder $\log \varepsilon = 3{,}623$ in guter Übereinstimmung mit den von Olerup (11) unter denselben Versuchsbedingungen aber mit einer ganz anderen Apparatur erhaltenen Werten $\varepsilon = 4\,226$ bzw. $\log \varepsilon = 3{,}626$.

Schliesslich wurde die auf S. 34 erwähnte Bestimmung der Abbleichungsgeschwindigkeit von Phenolphtalein bei grossem Überschuss von Natronlauge als Prüfungsmethode herangezogen. Die Versuchslösung hatte die Zusammensetzung 0,0003-m Phenolphtalein + 0,1-m NaOH + 0,1-m Na_2SO_4 und das benutzte Licht die Wellenlänge 436 mμ. Die Versuchstemperatur war 20°,0 C. Die fragliche Abbleichungsreaktion führt zu einem Gleichgewicht, und die komplexe Geschwindigkeitskonstante k, d. h. die Summe der monomolekularen Konstanten für die beiden entgegengesetzten Reaktionsrichtungen, kann nach der Formel

$$k = \frac{1}{t_2 - t_1} \cdot \log \frac{E_1 - E_j}{E_2 - E_j}$$

berechnet werden. (Vgl. Bodforss u. Leden (2).) E_1, E_2 und E_j sind die Extinktionswerte nach t_1 und t_2 Minuten, bzw. beim Gleichgewicht. Sie wurden nach S. 38—39 bestimmt. Schon

Tabelle 2. Die komplexe Geschwindigkeitskonstante k der Abbleichungsreaktionsreaktion des Phenolphtaleins bei Überschuss von Natronlauge. Versuchslösung:

0,0003-m Phenolphtalein + 0,1-m NaOH + 0,1-m Na_2SO_4.
Temp. 20°,0 C. Konstanten von Punkt zu Punkt berechnet.
Beim Gleichgewicht: $a_j = 116{,}6$.

Zeit t in Min.	Brücken-ablesung	$k \cdot 10^2$	Zeit t in Min.	Brücken-ablesung a	$k \cdot 10^2$
1,50	785,1	3,54	19,51	357,1	3,69
4,75	701,3	3,76	23,22	299,4	3,58
7,25	631,2	3,56	26,28	262,2	3,57
9,98	560,0	3,57	30,00	226,3	3,61
13,23	481,8	3,58	34,62	192,9	3,64
16,15	419,1	3,58	40,20	165,2	3,62
19,51	357,1		46,75	145,1	

Tabelle 3. Dieselbe Geschwindigkeitskonstante wie in Tab. 2, von den ersten t—a-Werten aus berechnet.

Zeit t in Min.	Brücken-abl. a	$k \cdot 10^2$	Zeit t in Min.	Brücken-abl. a	$k \cdot 10^2$	Zeit t in Min.	Brücken-abl. a	$k \cdot 10^2$
1,50	785,1	—	15,50	433,8	3,59	31,12	217,4	3,60
2,58	756,9	3,67	16,15	419,1	3,60	32,17	209,2	3,61
3,42	736,1	3,55	17,00	402,2	3,60	33,35	200,7	3,61
4,75	701,3	3,54	18,00	383,4	3,60	34,62	192,9	3,61
5,58	680,1	3,52	18,83	367,6	3,61	36,05	184,3	3,61
6,25	659,5	3,60	19,51	357,1	3,60	38,17	174,2	3,60
7,25	631,2	3,64	20,45	340,9	3,61	40,20	165,2	3,61
8,07	608,7	3,65	21,33	326,1	3,62	42,01	158,6	3,62
9,07	583,8	3,62	22,35	311,5	3,61	43,10	154,6	3,62
9,98	560,0	3,62	23,22	299,4	3,61	46,75	145,1	3,61
10,63	543,0	3,63	24,22	287,6	3,60	47,00	143,1	3,66
11,67	520,6	3,58	25,25	274,4	3,61	49,48	138,7	3,64
12,23	506,1	3,60	26,28	262,2	3,61	51,45	135,2	3,65
13,23	481,8	3,61	27,53	248,3	3,62	55,58	129,3	3,68
14,00	464,3	3,61	28,50	239,8	3,61	61,18	123,7	3,76
14,83	447,2	3,60	30,00	226,3	3,61			

nach einer Stunde hatte sich die Extinktion dem Gleichgewichtswert E_j bis auf 7 % angenähert, E_j wurde dann nach mehreren Stunden ermittelt.

In den Tabellen 2 und 3 sind die gefundenen k-Werte zusammengestellt. Diejenigen der ersten Tabelle sind von Zeitpunkt zu Zeitpunkt berechnet, die der zweiten sind alle auf $t_1 = 1{,}50$ Min. bezogen. Die gute Konstanz von k gibt noch eine Stütze für den Schluss auf die Proportionalität zwischen Lichtintensität und Sekundäremissionsstrom.

Zur *Monochromatisierung* des aus der Quecksilberlampe emittierten Lichtes diente in erster Hand ein Blaufilter für die Strahlung $\lambda = 436$ mμ (Zeiss' Monochromatorfilter C für Quecksilberlicht). Die in unserer Arbeit benutzten cäsiumbelegten Multiplikatorzellen sind aber auch für rotes Licht empfindlich, und Vorversuche mit einem Handspektroskop zeigten, dass das Blaufilter aus dem Quecksilberlicht noch eine rote Linie durch-

lässt. Diese Tatsache stimmte damit überein, dass wenn nach dem Blaufilter ein Zeiss' Gelbfilter (Zeiss' Monochromatorfilter A für Quecksilberlicht $\lambda = 576{,}9—579{,}0$ mμ) eingeschaltet wurde, das nach den Absorptionskurven alles Licht mit einer Wellenlänge < 550 mμ und also auch die Linie 436 mμ absorbiert, aber grosse Teile des Spektrums mit $\lambda > 550$ mμ durchlässt, die durch beide Filter gegangene Strahlung einen, wenn auch schwachen Sekundäremissionsstrom hervorrief. Das rote Licht konnte aber mit Hilfe einer 2 cm dicken Schicht einer einmolaren Kupferchloridlösung ganz absorbiert werden. Wenn eine Küvette mit einer solchen Lösung nach den kombinierten Gelb- und Blaufiltren in den Strahlengang eingeführt wurde, ging der Emissionsstrom nämlich auf Null hinunter. Zur Monochromatisierung war also ein Blaufilter + eine $CuCl_2$-Lösung der erwähnten Art vor jeder Zelle zu benutzen. Das Kupferchlorid kann mit praktisch demselben Rotabsorptionseffekt durch das Sulfat ersetzt werden. Dies hat den Vorteil, eine erheblich kleinere Schwächung der gewünschten Strahlung $\lambda = 436$ mμ hervorzurufen.

Zum Schluss möchten wir gern hervorheben, dass Herr Fil. Kand. L. Stigmark die elektrische Ausrüstung unseres Apparates mit grosser Geschicklichkeit konstruiert hat. Wir danken ihm herzlich dafür.

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The Photochemical Oxidation of Alcohols in the Presence of Benzophenone.

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As was shown by Ciamician and Silber (1) in 1900, solutions of benzophenone in certain alcohols, when exposed to sun-light, separate benzopinacone with the simultaneous dehydration of the alcohol to the corresponding aldehyde or ketone. This reaction was further investigated by Böeseken and his pupils (2, 3) who found that in the presence of oxygen the reaction takes a different course, the benzophenone remaining unchanged and only serving as a catalyst to the photochemical oxidation of the alcohol. A discussion of the mechanism of this reaction, based mainly on the experimental results of Böeseken and Cohen, was given by the author in a previous paper (4). The ideas arrived at could be applied also to the photo-sensitizing action of benzophenone in the autoxidation of aliphatic aldehydes (5) and thus, indirectly, led to the formulation of a chain mechanism for the autoxidation of aldehydes.

A later investigation by Berthoud (6) on the photochemical oxidation of ethyl alcohol, however, led to results differing in important respects from those obtained by Böeseken and Cohen. In an attempt to clear up these differences the present work was undertaken.

Previous Investigations.

In the paper cited the author gave a rather detailed account of the results obtained by Böeseken and his pupils. Here

only those among them will be mentioned that are of particular importance in the present connection.

1. Under given conditions of illumination the amount of alcohol reacting in unit time is the same whether oxygen is present or not. In the latter case we have the reaction of Ciamician and Silber:

$$2\,(C_6H_5)_2CO' + RCH_2OH = (C_6H_5)_2C(OH)\cdot C(OH)(C_6H_5)_2 + \\ + RCHO.^1$$

In the former case we have, according to Böeseken, formation of aldehyde (or ketone) and water:

$$2\,(C_6H_5)_2CO' + RCH_2OH + O_2 = 2\,(C_6H_5)_2CO + \\ + RCHO + H_2O.$$

The oxidation velocity is the same in air as in oxygen (7).

2. Experiments in the light of a mercury arc showed that increasing the benzophenone concentration above a certain value does not lead to an increase in the reaction rate. This is due to the fact that under these conditions the active light is completely absorbed. Under these conditions the rate of pinacone formation is the same in a series of different alcohols (ethyl, n-propyl, isopropyl, n-butyl and isoamyl). In certain other alcohols, e. g. in methyl alcohol, the rate is lower. Experiments with mixtures of ethyl alcohol and benzene showed that the alcohol has to be diluted about 10 times before the rate of pinacone formation begins to drop.

3. Experiments with substituted benzophenones and other aromatic ketones showed that for at least 3 of these the rate of pinacone formation in ethyl alcohol was the same, within limits of error, as for benzophenone. For all the others the rate was lower.

4. The rate of reaction was found to be proportional to the intensity of illumination.

These results indicate that in a large number of the cases investigated the reaction obeys the photochemical equivalence law, whereas in the rest of the cases the quantum yield is

[1] An accent after the formula denotes that the molecule has been activated by light absorption.

less than 1, owing to the fact that a certain fraction of the light absorbing benzophenone molecules are deactivated before they have time to react with the alcohol. In contrast to this, Berthoud, who made a direct determination of the quantum yield of the sensitized oxidation of ethyl alcohol, found that 18 molecules of oxygen reacted for every light quantum absorbed. His other results, as well, seemed to support the view that he was dealing with a chain reaction. He found that the reaction showed a pronounced induction period of varying length but generally amounting to half an hour, in the course of which the rate would rise, e. g., from 1,1 to 4,5 cc of oxygen in 5 minutes. If the light was turned off for about 10 min., about the same length of time was again required for the rate to reach its maximum value, and this value was not always the same as before but was occasionally as much as 50 % lower. On the whole his results were not reproducible and he speaks of "unexplainable variations". When the light was shut off he sometimes observed a pronounced photochemical after-effect, but sometimes it was less pronounced or altogether absent. The temperature coefficient was found to be relatively high, 1.7 for a 10° rise in temperature. As for the influence of oxygen pressure, the rate was found to decrease with increasing pressure. The values obtained with pure oxygen, a 50 % mixture of oxygen and nitrogen, and air, were in the ratio of 1 : 1.3 : 1.7.

Berthoud only measured rates of oxygen absorption. His experimental arrangements are not described in detail.

Experimental.

In the author's own experiments, solutions of benzophenone in different alcohols were shaken with oxygen or air in the light of a mercury arc. The apparatus used has been described elsewhere (8). It consisted of a shaking tube, made of glass or quartz, which could be mechanically shaken while immersed in a water bath with a quartz window. Before reaching the window the light had to pass a glass plate which completely absorbed the shorter wave-lenghts including the line at 313 mμ. Thus only the long wave-length region of the ultraviolet,

mainly the strong line at 366 mμ was used. In this region, light absorption causes only an activation of the benzophenone molecule, probably resulting in a splitting of the double bond of the carbonyl group (cf. ref. 4), whereas shorter wave-lengths may cause a primary dissociation of the molecule to take place. For the experiments with pure oxygen of varying pressure a thick-walled shaking tube of a somewhat different type was used. It was made of glass and consisted of a wider part (length about 11 cm, inner diameter 19 mm, wall-thickness 4 mm) and a narrower tube, 27 cm long, with the upper end shaped to hold rubber tubing. The length of this tube prevented the liquid from coming into contact with the rubber tubing during the shaking. At oxygen pressures up to 2 atm. the tube was connected by means of thick-walled rubber tubing with a glass bottle of the Woulff type with two nipples, which was immersed in the water bath and had a volume of about 530 cc. The bottle in its turn was connected with an open mercury manometer and, by means of glass stopcocks, with the oxygen tank and an oil pump. After filling the apparatus with oxygen by repeated evacuation, all rubber tubes connecting it with the atmosphere were closed with large-size screw compressor clamps, which proved the only way to get the system tight. Since its total volume amounted to more than 600 cc, the oxygen absorbed during a run only caused a relatively unimportant pressure drop. The reaction rate was determined by analysis of the oxidised solution. All connections between rubber and glass were secured by means of aluminium ribbons ("Bindex" clamps). Experiments at pressures above 2 atmospheres were made by filling the shaking tube with oxygen of the desired pressure, which was read off on a standardized spiral manometer, and closing the connecting rubber tubing with a screw compressor clamp placed a few mm from the end of the glass tube. These pressure measurements must be considered less accurate than the rest. The pressure drop during the run was calculated from the analysis.

For the first experiments, two different D. C. mercury arc lamps were used, one of the ordinary horizontal type, the other a water-cooled Kromayer lamp. Both were placed immediately in front of the thermostat window. Current and voltage were

kept as constant as possible by means of a regulating resistance. The later experiments were made with a vertical A. C. burner (L K 700) from *Lumalampan AB*, Stockholm, which was kindly placed at my disposal by the manufacturers. In order to eliminate variations in the city current, the lamp was burned in series with a regulating resistance as well as with a battery of six hydrogen-filled iron resistance tubes, connected in parallel and each transmitting about 1.45 amp. Two of these were only used at the start and were shunted out two minutes after lighting the lamp. The stated regulating voltage of the tubes was from 15 to 40 volts. By regulating the outside resistance, the voltage across the tubes was kept as nearly as possible at 32 volts. Intensity measurements showed that the intensity became constant within one percent about 15 minutes after lighting the lamp and that a change in the tube voltage of 1 volt changed the intensity by about ½ %. The lamp was placed in a fixed position 10 cm from the thermostat window and was inclosed in a lamp box with ventilating arrangements and two glass windows at right angles to each other. Both windows were cut from the same glass plate and were stabilized by 12 hours irradiation with the mercury arc before use (9). One of the windows faced the thermostat; through the other the light could be brought to fall on a Moll micro-thermoelement, placed in a fixed position 55 cm from the lamp and connected to a mirror galvanometer. Immediately in front of the thermoelement was a 1-cm quartz cell with distilled water and a 3-cm cell of the same material with a solution containing 23.0 % $CoSO_4$ + 0.62 % $CuSO_4$. Spectro-photographic extinction measurements showed that this filter transmits about 50 % at 366 mμ as against only about 1 % at 405 mμ. Since for lamps of this type the line at 366 mμ is more than twice as strong as that at 405 mμ, and the correction for red and infrared light was found to be only about 0.6 % of the galvanometer deflections, these deflections could be taken as a measure of the active light. On this basis reaction rates determined at different times could be corrected for the decrease in the intensity of the lamp with time.

Results.

The investigation was started with orienting experiments with a number of different alcohols, the main purpose being to find out what products were formed in the reaction. In these experiments, which were carried out both in air and in oxygen, the rate was found to be lower in oxygen than in air, in accordance with the results of Berthoud. Under these circumstances, the most urgent task appeared to be to find an explanation of this curious phenomenon. Systematic experiments on the influence of oxygen pressure were therefore carried out in a special case, namely the oxidation of isopropyl alcohol.

As regards the nature of the reaction products, this question has not previously been investigated, but it has been tacitly assumed that the alcohol is oxidized to water and the corresponding aldehyde or ketone. This is not the case, however. Secondary alcohols are oxidized almost quantitatively to ketone and hydrogen peroxide. With primary alcohols the corresponding reaction takes place, but there is also a side-reaction leading to the formation of carboxylic acid.

The hydrogen peroxide formed was determined iodimetrically by titration with 0.1 N thiosulfate. This determination could not be carried out with accuracy in alcohol when air was present. In that case the values tend to be high and there is a rapid shift of the end point. The determination was therefore carried out in the following way: 5 cc of 5 N-H_2SO_4 + 2 cc of saturated KI-solution were introduced into a small test tube (120 × 20 mm), and the sample solution (generally 10 cc) + 10 cc 95 % ethyl alcohol into a larger tube (130 × 32 mm). Carbon dioxide was bubbled through both solutions in such a way, that the current first passed the smaller tube. After 10 min. the smaller tube was tilted so that its contents were transferred to the larger tube. The titration was carried out 10 min. later with the carbon dioxide still bubbling through the solution. Determinations on hydrogen peroxide solutions of known strength showed the correctness of the results obtained by this method. Thus 2 cc of a water-solution of

H_2O_2 + 20 cc H_2O, with the above-mentioned quantities of KI and H_2SO_4, on titration after 10 min. with starch as an indicator, gave 7.60 cc of thiosulfate. Exactly the same value was obtained, by the method described above, with 2 cc of the H_2O_2-solution + 20 cc of 95 % alcohol. In the same manner, 5 cc of another H_2O_2-solution gave, in water, 19.26 cc, in alcohol, 19.23 cc.

Determinations of carboxylic acid formed were made either on an aliquot portion of the solution or before the peroxide determination, by titration with 0.1 N carbon dioxide-free sodium hydroxide solution and phenolphthalein.

The fact that the peroxide formed is hydrogen peroxide and not some organic peroxide could be shown in two cases by a method which has been used by the author on a previous occasion (10) and which is based on the solubility of hydrogen peroxide in water. The following results were obtained:

I. 10 cc of a solution of 2 g of benzophenone + 7.7 g of benzhydrol in 20 cc of benzene were oxidised until 8.19 cc = 0.342 millimoles of O_2 had been absorbed. The solution was transferred to a separatory funnel and shaken twice with 20-cc portions of water. On iodimetric titration, the water layers consumed 8.35 and 0.09 cc of 0.0796-N thiosulfate, respectively, corresponding to a total of 0.336 millimoles of H_2O_2, or 98 % of the oxygen absorbed.

II. 10 cc of a 7.5 % solution of benzophenone in benzyl alcohol were shaken with oxygen until 21.32 cc = 0.893 millimoles had been absorbed. 4 cc were mixed with benzene and shaken out twice with an equal volume of water. The water layers consumed 8.91 and 0.10 cc of thiosulfate, respectively, corresponding to 0.895 millimoles of H_2O_2 for the whole solution = 100 %.

Of the other alcohols tried, two were secondary, namely, isopropyl alcohol and sec. butyl alcohol. A considerable number of experiments with isopropyl alcohol gave, on the average, a peroxide yield of 99.6 % (variations between 99.3 and 100.0 %). In addition, there was formed about 0.5 % of acid. One experiment with secondary butyl alcohol gave a yield of 109 % of peroxide. The titration was carried out in air, which probably accounts for the high value.

With ethyl alcohol experiments were made in oxygen and air at 15, 25, and 35°, and at different light intensities. The

peroxide yield varied between 54 and 65 %, whereas the amount of acid, in equivalents per mole of oxygen, generally varied in the opposite direction (between 61 and 48 %) so that the sum remained fairly constant (variations between 112 and 121 %, average 118 %). The total amount of these reaction products is thus too high to be explained on the basis of the equations: $CH_3CH_2OH + O_2 = CH_3CHO + H_2O_2$, and $CH_3CH_2OH + O_2 = CH_3COOH + H_2O$. It therefore appears probable that the oxidation of the alcohol is in this case accompanied by a partial reduction of the benzophenone, a case which would be somewhat analogous to the formation of traces of stilbene and benzoic acid on illumination of benzaldehyde, reported by Raymond (11). No attempt has so far been made to corroborate this view. Similar conditions are found for isoamyl alcohol. One experiment gave 48 % acid and 74 % peroxide (titration in air). In the experiment with benzyl alcohol described above, 4 % of acid were formed in addition to the 100 % of hydrogen peroxide.

In the case of ethyl alcohol it was shown that the formation of acid is not due to a secondary oxidation effect of the hydrogen peroxide formed. Thus, for instance, the same amounts of peroxide and acid are formed if a quantity of concentrated hydrogen peroxide is added to the solution before the experiment, equal to twice that formed during the run.

Analytical determinations of the carbonyl compound formed in the oxidation were only made in the case of isopropyl alcohol. The acetone was determined by a spectro-photometric method described by the author in an earlier publication (12). The isopropyl alcohol present was found to interfere with the determination, and it therefore became necessary to effect a separation. This was done by mixing 2 cc of the sample with 10 cc of acetone-free methanol, 5 cc of water, and 2 drops of glacial acetic acid (to minimize the oxidation effect of the H_2O_2 present), and subjecting the mixture to fractional distillation using the apparatus described in the paper cited. In this way the benzophenone was removed along with the isopropyl alcohol. The distilling flask had a volume of 50 cc. Of the distillate, amounting to about 3.9 cc, 2 or 3 cc was

diluted with water to a suitable volume and 1 cc of the resulting solution used for the analysis. Distillation experiments with known amounts of acetone gave the following results:

Acetone used 0.1158 millimoles			
Distillation time, minutes	4.5	15	16
Acetone found, millimoles	0.1124	0.1144	0.1155
» » %	97.2	98.8	99.7

In carrying out analyses by this method the distillation time was always more than 20 minutes. A blank determination made under these conditions in the presence of 0.1 millimole of hydrogen peroxide gave 0.001 millimole of acetone. This was not corrected for. The results obtained are given on page 56.

The Rate of Reaction.

As an example of the results obtained, the following experiment may be cited, performed with a 5 % solution of benzophenone in ethyl alcohol at 20°. The figures represent the quantities of oxygen absorbed during the first and second minutes of illumination and the mean values during subsequent 2-minute periods:

Min.	1	2	3—4	5—6	7—8	9—10	11—12	13—14	15—16	17—18	19—20
cc/-min.	0.37	0.34	0.355	0.355	0.375	0.36	0.375	0.365	0.355	0.355	0.36

As will be seen, the rate at once reaches its full value and remains constant throughout the run. As a rule, however, the absorption during the first minute was a few hundredths of a cc below the average during the run. Special experiments indicated the existence of a photochemical after-effect of a similar magnitude. Apparently, however, the reaction caused by the light takes place in the course of a few seconds. In the later experiments with isopropyl alcohol, however, results were at first obtained that, to a certain extent, resembled those reported by Berthoud, the rate rising, for instance, from 0.44 to 0.55 cc/min. in the course of the first 30 minutes, and then remaining constant. This could be traced to the presence of impurities. 1 kg of the isopropyl alcohol used

(a 99 % product of American origin) was divided into 7 fractions by distillation at atmospheric pressure using a YOUNG distilling column with 5 bulbs. Already fraction 3 (Bp. 82.2—82.25° corr.), when oxidized in the presence of pure benzophenone, gave only a very slight induction period and the same mean reaction rate, within limits of error, as the following fractions that did not show any induction period. The final experiments were made with fractions 4 to 6 (Bp. 82.25—82.4°). They were free from acetone.

For these experiments, two different benzophenone preparations were tried, namely *Kahlbaum's* and *Merck's* "for scientific purposes", the latter stated to have a melting point of about 48°. A 7.5 % solution of the former preparation in pure isopropyl alcohol at 25° showed an initial oxidation rate of 0.58 cc/min., which in the course of 10 minutes rose to 0.65 cc/min. and then remained constant. Under the same conditions the latter preparation at once gave a constant oxidation rate of 0.79 cc/min. When the former preparation was subjected to fractional distillation at a pressure of about 3 mm, some volatile impurities were first removed. The remainder was divided into two fractions, both distilling at 138—140°, and giving reaction rates of 0.72 cc/min. (No. 1) and 0.67 cc/min (No. 2) respectively, without any induction period. As appears from this, the preparation contained two kinds of impurities: some volatile impurity causing the induction period, and some other impurity, less volatile than benzophenone itself, causing a lowering of the final oxidation rate. Probably the second impurity was a light-absorbing, photochemically inactive substance, e. g. phenyl naphthyl ketone. The *Merck* preparation, on the other hand, was probably free from impurities. When it was subjected to the same process of purification the fractions obtained both gave the same rate as the original substance. For the final experiments only this preparation was used.

In view of these results it seems probable that BERTHOUDS experiments were influenced by the presence of impurities.

Special experiments showed that the rate of oxidation was the same for solutions containing 5 and 10 grams of benzophenone in 100 cc of alcohol, whereas with 2.5 grams the

rate was 11 % lower. Although 5 grams was therefore sufficient for complete light absorption, 7.5 grams was used throughout.

The results obtained in preliminary experiments with different alcohols are summarized in Table 1. They were made with 10 cc of solution at 20°, both in oxygen and in air. In the latter case the rate was higher from the start and continued to rise as the oxygen was consumed, finally dropping to 0 when about 8 cc had been absorbed. In these experiments both the shaking tube and the gas burette were filled with air, and the connecting rubber tubing had a bore of only a few millimeters, so that no appreciable diffusion could take place. The volume of the tube was 44 cc. For the experiments in air, the table gives the initial oxidation rate as well as the maximum value observed during the run.

Table 1.

Rates of Oxidation in cc/min.

	Oxygen	Air Initial rate	Air Maximum rate
Ethyl alcohol	0.31	0.57	0.63
Isoamyl alcohol	0.27	0.46	0.50
Benzyl alcohol	0.80	0.61	decreasing
Isopropyl alcohol	0.265	0.41	0.48
Sec.butyl alcohol	0.24		
Benzhydrol, abt. 30 %, in benzene	0.25		

The alcohols used were commercial preparations that had not been purified and the results cannot, therefore, be regarded as final. The table shows, however, that different alcohols are oxidized at approximately the same rate, in agreement with Cohen's results for the rate of pinacone formation. Berthoud's results with regard to the influence of oxygen pressure on the rate of oxidation of ethyl alcohol are found to apply to other alcohols as well. In both respects, however, benzyl alcohol forms an exception. In oxygen it reacts considerably more rapidly than the other alcohols, and in air its rate of oxidation is lower than in oxygen and decreases steadily during the run.

The benzyl alcohol had a faint smell of benzaldehyde, but purifying the alcohol by shaking successively with bisulfite solution, dilute sodium hydroxide, and water, drying over calcium chloride, and distilling, did not change the results.

Systematic Experiments with Isopropyl Alcohol.

For a closer study of the dependence of the reaction rate on the oxygen pressure, isopropyl alcohol was selected, since this alcohol offers both practical and theoretical advantages. As shown above, it represents a particularly simple case, the peroxide yield amounting to almost exactly 100 %. The rate of oxidation was determined by titration. The temperature was 25°, and the solutions shaken had a volume of 10 cc. The results are summarized in Table 2, where column 2 gives the light intensity (the galvanometer deflection in cm.), and column 3 the oxygen pressure obtained by deducting the calculated vapour pressure (43 mm of mercury) (13) from the total pressure. Column 6 gives the observed reaction rate in

Table 2.

No.	Intensity	Pressure, atm.	Time, min.	H_2O_2 millimoles	v_{obs}	$v_{calc.}$	Acetone, millimoles
1	5.40	4.93	25	0.191	7.74	7.63	0.165
2	5.38	3.49	25	0.246	10.06	10.04	0.230
3	5.29	1.884	25	0.373	15.5	15.5	
4	5.50	0.938	25	0.591	23.6	22.9	0.588
5	5.30	0.899	25	0.544	22.6	23.4	
6	5.31	0.404	25	0.758	31.4	31.3	
7	5.29	0.217	25	0.862	35.8	36.0	0.863
8	5.26	1.945	43	0.259	6.30	6.39	
9	5.28	0.908	26	0.288	11.5	11.4	
10	5.30	0.220	25	0.579	24.1	24.1	
11	5.34	1.947	54	0.131	2.61	2.67	
12	5.36	0.919	37	0.182	5.05	4.96	
13	5.32	0.228	25	0.274	11.63	11.69	

mole $\times 10^{-6}$ per minute, corrected to a galvanometer deflection of 5,50 cm. As shown by column 7, the observed values agree within limits of error with those calculated from the formula $v = \frac{45.6}{p + 1.05}$. This is also shown graphically in Fig. 1, where the product of pressure and reaction rate has been plotted

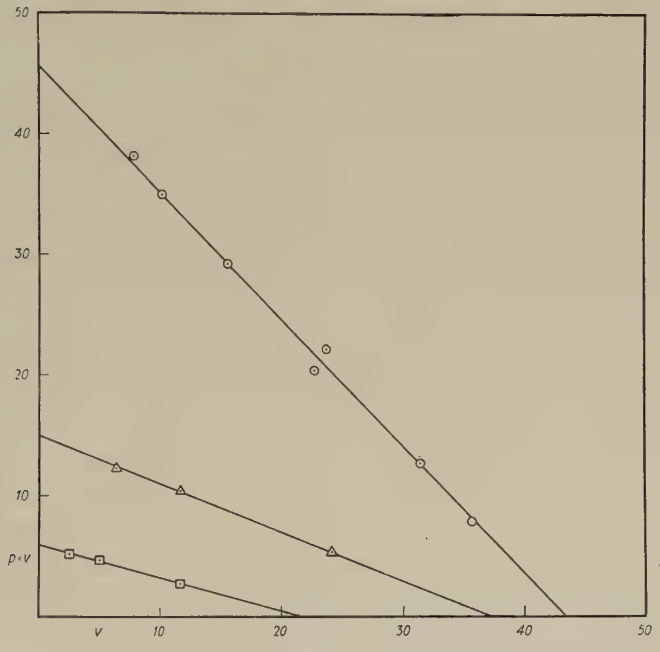

Fig. 1.

against the rate. Column 8 gives the results of the acetone determinations. In experiments 4 and 7 the agreement between the figures for acetone and hydrogen peroxide is very good, but in experiment 1 it is rather poor, probably owing to the fact that acetone escaped with the oxygen when the tube was opened. In experiment 2, where the tube was cooled in a cooling mixture before opening, the agreement is better. The figures may serve to show that the same reaction takes place at high as at low pressures and that only the rate varies. Some experiments in air at atmospheric pressure indicated, however, that this is changed at very low oxygen pressures.

In one such experiment, for instance, in which, during the later part of the run, a constant low oxygen supply was maintained in the shaking tube by diffusion from the oxygen-filled burette, the amount of acetone formed was 0.751 millimoles but the amount of oxygen absorbed only 0.457 millimoles. The peroxide yield was exceptionally low (0.440 millimole = 96.4 %) and the acid yield exceptionally high (3.0 %). There was no sign of pinacone formation. The point will be investigated further.

The series of experiments in Table 2 included a number of runs where the isopropyl alcohol had been diluted with tertiary butyl alcohol in the ratio of 3 : 7 (Nos. 8—10) and 1 : 9 (Nos. 11—13). The purpose of these was to study the influence of the alcohol concentration on the reaction rate, especially at higher oxygen pressures. In one way tertiary butyl alcohol is not an ideal diluent, since it is itself oxidized under these conditions, although very slowly, but its chemical similarity with isopropyl alcohol is an advantage. Thus the solubility of oxygen in the two alcohols should be about the same, which is of importance in the present case. The vapour pressures at 25° differ by only 2 mm. The tertiary butyl alcohol used was purified by crystallization from the melt. The rate of oxidation in the presence of benzophenone was found to be, in oxygen, 0.02 cc/min., in air, 0.047 cc/min., as against 0.80, and 1.30, for isopropyl alcohol under the same conditions. As shown by these figures, the dependence of the oxidation rate on the oxygen pressure is particularly marked in the case of tertiary butyl alcohol.

As appears from Table 2 and Fig. 1, the observed values for the rate of oxidation of 30 % and 10 % isopropyl alcohol solutions can be represented by two straight lines, viz.

$$v = \frac{15}{p + 0.403}, \text{ and } v = \frac{5.95}{p + 0.281}.$$

The number of points is too small to enable the lines to be drawn with any considerable degree of certainty, but a sufficiently accurate extrapolation to high oxygen pressures may be made. This extrapolation shows that the rate of oxidation

under these conditions is not far from proportional to the alcohol concentration. This would require $v=\frac{13.7}{p}$, and $v=\frac{4.6}{p}$, respectively. That the observed values of the constants are both about 1.3 units higher may probably be ascribed to the oxidation of the tertiary butyl alcohol.

In connection with the experiments recorded in Table 2, determinations were also made of the rate of pinacone formation under the same conditions of illumination. In one case the shaking tube was connected to the gas burette and both were filled with tank nitrogen, in the other case the procedure was that employed in determinations at varying oxygen pressures, only the system was filled with carbon dioxide by repeated evacuation. In both cases the shaking time was 25 minutes, and the rate was measured by determining the amount of acetone formed. The first experiment (galvanometer deflection 5.44 cm) gave 0.594 millimoles, the second (deflection 5.29 cm) 0.580 millimoles, corresponding to corrected reaction rates of 0.0240 and 0.0241 millimoles per minute, respectively. The rate was therefore only 55 % of the value obtained by extrapolating the results of the oxidation experiments to zero oxygen pressure, viz. 0.0434 millimoles/min. Since in both cases a certain amount of oxidation took place during the run, a small correction should be applied which would lower the results still further. In the first two minutes of the first experiment there was an absorption of 0.42 and 0.05 cc, respectively, corresponding to a total of 0.020 millimoles of oxygen. In the second, a titration after the run revealed, that 0.035 millimoles of H_2O_2 had been formed. In view of what has been said above concerning acetone formation at very low oxygen pressures, the magnitude of the correction cannot be stated with certainty. The results seem to indicate, however, that the maximum amount of acetone formed in the presence of oxygen is twice that formed when oxygen is absent, conditions of illumination being equal.

Certain measurements of the rate of pinacone formation in isopropyl alcohol, made in connection with the preliminary experiments, tend to support this conclusion. In these experiments, which will not be described in detail, the rate was

measured by determining the amount of pinacone formed. The rate of pinacone formation in an atmosphere of carbon dioxide at 20° (on the average 0.0150 millimole/min.) was almost the same as the rate of oxidation in oxygen at atmospheric pressure (0.0145 millimole/min.). According to the formula given above, however, the latter rate is, at 25°, almost exactly half (51 %) of the extrapolated maximum rate.

These experiments also included an approximate determination of the quantum yield. For this purpose the rate was compared with that of a reaction with known quantum yield, viz. the decomposition of uranyl oxalate (14). The light source was a KROMAYER lamp, and the light was filtered through a 3-cm quartz cell with 2-molar cobalt sulfate solution and a glass plate. The light used therefore mainly consisted of the mercury line at 366 mμ. In order to get complete absorption of this line by the uranyl oxalate solution it was necessary, however, to use a higher concentration (0.05 mole/lit) than in the work of LEIGHTON and FORBES (0.01 mole/lit.), and since the quantum yield is known to vary somewhat with the concentration, the determination can not be regarded as very accurate. Furthermore, the benzophenone and the isopropyl alcohol had not been subjected to purification. The accuracy was sufficient, however, to show that the oxidation of isopropyl alcohol is not a chain reaction. The rate at 20° and an oxygen pressure of 1 atm. corresponded to a yield of 0.54 molecules of oxygen per quantum.

The Reaction Mechanism.

The results obtained can be explained on the basis of the following reaction scheme:

$$(C_6H_5)_2CO + h\nu = (C_6H_5)_2\dot{C}{-}O{-} \qquad (1)$$

$$(C_6H_5)_2\dot{C}{-}O{-} + (CH_3)_2CHOH = (C_6H_5)_2\dot{C}{-}O{-}H + (CH_3)_2\dot{C}{-}O{-}H \qquad (2)$$

$$2\,(C_6H_5)_2\dot{C}{-}O{-}H = (C_6H_5)_2C(OH)\cdot C(OH)(C_6H_5)_2 \qquad (3)$$

$$2\,(CH_3)_2\dot{C}{-}O{-}H = (CH_3)_2CHOH + (CH_3)_2CO \qquad (4)$$

$$(C_6H_5)_2\overset{/}{C}\text{—}O\text{—} + O_2 = (C_6H_5)_2CO + O_2 \quad (5)$$

$$(C_6H_5)_2\overset{/}{C}\text{—}O\text{—}H + (CH_3)_2\overset{/}{C}\text{—}O\text{—}H + O_2 = (C_6H_5)_2CO + (CH_3)_2CO + H_2O_2 \quad (6)$$

Reactions (1)—(4) determine the reaction in the absence of oxygen and give a quantum yield of 0.5 molecules of pinacone and acetone per hν. With regard to reaction (1), the reader is referred to an earlier publication (4). The assumption underlying reaction (5), that oxygen has a specific power of deactivating light-activated benzophenone molecules, seems inevitable to explain its retarding effect on the oxidation of the alcohol. Since this reaction competes with reaction (2), the effect should be more pronounced, the less easily dehydrated the alcohol is. This probably explains that no retarding effect is observed in the oxidation of benzyl alcohol, and that the effect is particularly marked in the case of tertiary butyl alcohol.[1]

In the presence of oxygen, reaction (6) must be assumed to proceed at such a rate that reactions (3) and (4) are prevented from taking place. Probably the formation of HO_2 radicals is an intermediate step in this reaction.

The same reaction scheme may be used, with slight modifications, to explain the observation, recently reported by Schönberg and Mostafa (15), that benzopinacone and isopropyl alcohol are formed when a solution of benzhydrol in acetone is exposed to sun-light in a sealed tube. The absorption spectra of the two substances show that the light must be absorbed by the acetone. The following reactions may be assumed to take place:

$$(CH_3)_2CO + h\nu = (CH_3)_2\overset{/}{C}\text{—}O\text{—} \quad (1\,a)$$

$$(CH_3)_2\overset{/}{C}\text{—}O\text{—} + (C_6H_5)_2CHOH = (CH_3)_2\overset{/}{C}\text{—}OH + (C_6H_5)_2\overset{/}{C}\text{—}OH \quad (2\,a)$$

From this point the reaction would proceed according to (3)

[1] In this connection it may be recalled, that benzyl alcohol is considerably more effective as an inhibitor in autoxidation reactions than ethyl and isopropyl alcohol, which is connected with the ease with which it is dehydrated. — In the case of tertiary alcohols, reaction (2) should be replaced by some other dehydration reaction. According to Cohen (2), unsaturated compounds are formed when tertiary alcohols are irradiated in the presence of benzophenone.

and (4). In support of reaction (1 a) the fact may be cited that, under certain conditions, irradiation of acetone gives rise to the formation of diacetone alcohol, $(CH_3)_2C(OH)CH_2COCH_3$ (16).

In order to explain the lower rate of pinacone formation in certain alcohols, like methanol, as well as for other reasons, it is necessary to assume that, besides reaction (5), some other process of deactivation plays a part in the reaction. If it is assumed that this is a spontaneous deactivation:

$$(C_6H_5)_2\overset{\diagup}{C}\!-\!O- = (C_6H_5)_2CO, \qquad (7)$$

the following equation is arrived at for the rate of reaction:

$$-\frac{d[A]}{dt} = \frac{k_1 I k_2 [A]}{k_7 + k_5 [O_2] + k_2 [A]},$$

where $[A]$ and $[O_2]$ denote the concentrations of alcohol and oxygen, respectively, and I the light intensity. Thus, in accordance with the experimental results, an equation is obtained which, for a given alcohol concentration, is represented by a straight line in the *v-pv*-diagram. However, this equation does not correctly represent the variation in the slopes of the different lines with the alcohol concentration, which shows that the assumption made with regard to the nature of the deactivation process (reaction 7) is too simple. Instead it must be assumed that deactivation may also take place in collisions with other molecules, and with a different degree of probability depending on the molecular species. The number of determinations is too small to test the formula arising out of these assumptions. Obviously, however, this formula, as well as the one given above, will reduce to $v = \frac{k[A]}{p}$ at sufficiently high oxygen pressures.

Some cases of inhibition by oxygen, that probably belong to the same class as the one described above, were discovered by Weigert in 1912 (17). He found that a 0.1 % quinine sulfate solution, when shaken with different mixtures of oxygen and nitrogen in the light of a mercury arc, was oxidized 30 times more slowly in pure oxygen than in a mixture containing 0.6 % of oxygen. Similar results were obtained with solutions

of some fluorescein dyes. In spite of the high intensity of illumination, the rate of reaction was in all cases very low (less than 1 cc of oxygen per minute), which makes it improbable that the reactions studied were chain reactions. The fluorescence exhibited by these substances shows that, just as in the case described above, the primary process on light absorption consists in raising the molecule to a higher electronic state, and not in a primary dissociation. The only reaction product identified by Weigert was hydrogen peroxide.

In the other known cases of oxidation reactions inhibited by oxygen, as in the oxidation of phosphorus, we are dealing with chain reactions, and the phenomenon is due to the power of oxygen, when present in too high a concentration, to disturb the normal course of the reaction chains. In the case of the oxidation of phosphorus, for instance, it has been shown to be associated with the simultaneous formation of ozone and hydrogen peroxide (Ref. 5).

In this connection reference should also be made to the quenching of fluorescence in solution by certain classes of substances (18), a process which is closely analogous to the one postulated above to explain the retarding effect of oxygen in the photo-sensitized oxidation of alcohols. This aspect will be given special attention in further work on this reaction. It may be recalled here, however, that, in the case of certain fluorescent substances, oxygen has been found to exert a specific quenching effect. In some of these cases, as with anthracene (19) and diacetyl (20), this effect has been shown to be connected with a chemical reaction in which oxygen is consumed, and in the rest of the cases this possibility is not excluded by the available experimental evidence. In the present instance, however, such an interpretation would not be in agreement with the experimental facts.

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Investigation of the Photographic Latent Image by Means of the Pressure Effect.

(Preliminary Report).

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The photographical material generally used is composed of a base upon which an emulsion, consisting of small silver halide crystals in gelatine, has been deposited. When this material is exposed in the normal manner, no directly visible change is observed; the image obtained is latent, but can be developed in a reducing solution (the developer). According to the varying degree of the exposure a more or less great number of silver halide grains per area unit are capable of being developed, and, if the developing time is sufficiently extended, these grains are completely reduced to silver, while the rest of the grains remain unchanged.

It was of great importance in the understanding of the nature of the latent image when The Svedberg (1) in the early twenties clearly demonstrated that the reduction of the individual grain starts from certain definite points (centres, nuclei) on the grain. As we furthermore know that the silver halide grains of the emulsion originally had a rather low sensitivity to light, which has been raised by a special "ripening process" in the course of manufacture, it is reasonable to suppose that certain "sensitivity specks" have been produced, and that under the influence of light during the exposure these specks are transformed into development nuclei. This

[1] H. Bäckström has planned and directed the work and written the manuscript. He is also responsible for the theoretical views. C. A. Bruno and M. Müller have carried out the experiments.

supposition has been confirmed by the work of SHEPPARD (2) and his collaborators. According to them, sensitivity specks arise during the ripening under the influence of small amounts of allyl thiocarbamide, which is found in photographically active gelatine; the sensitivity specks will consequently consist of silver sulphide and partly also of silver, the latter according to CLARK (3). During the exposure the sensitivity speck is increased by silver liberated by the action of light.

Not until GURNEY and MOTT (4), shortly before the outbreak of the present war, presented their theory, did there exist a satisfactory hypothesis concerning the mechanism at work in the transformation of sensitivity specks into development nuclei. The theory of GURNEY and MOTT explains the whole series of photographical effects from uniform premises. As this theory has a certain importance in connection with the conclusions of this article its principal points will be briefly recapitulated.

According to the modern conception of a silver halide crystal it consists of a lattice of silver and halide ions. Some of the silver ions, however, have left their places in the lattice and vagabond between the layers. The higher the temperature is, the greater number of silver ions are liberated from their places in this way.

In the exposure halide ions present in the lattice absorb light quanta, by which procedure one electron is liberated for each quantum absorbed. This absorption of light naturally takes place in parts of the crystal widely separated from each other. Under such circumstances, however, it is difficult to understand how the sensitivity speck grows into a development nucleus.

According to GURNEY and MOTT the electrons liberated by light move freely in the crystal until either they return to their original places, or they encounter the sensitivity speck, which serves as a kind of electron trap. The sensitivity speck becomes negatively charged by the captured electron and is therefore capable of attracting vagabonding silver ions. An electrolytic conduction is brought about and the ions are discharged at the speck, which is consequently increased by deposited silver. When the speck has grown large enough a development nucleus has been formed.

We have long known that exposures ($I \cdot t$) of the same length have not the same photographic effect for different values of light intensity (I) and of time of exposure (t), but that the efficiency reaches a maximum at a certain value of I (the optimum intensity) and is lowered by weaker as well as by stronger light.

The explanation of the lower efficiency at low intensities, in which we have a particular interest here, is supposed by WEBB and EVANS (5) to lie in the comparative unstability of the first small sensitivity specks. However, they gain in stability during the exposure as new silver is added to them and they increase in size. If the exposure takes place in very weak light, part of the silver supplied in the beginning will thus vanish from the speck before more stabilizing silver is supplied.

The Pressure Effect on the Sensitivity of Photographic Material.

POINDEXTER (6) has discovered a photographic effect consisting in the fact that a photographic material, which during the actual exposure is subjected to a heavy static pressure, will show less density after development than if the exposure has taken place in the absence of pressure (6—8). A few years ago this effect was made the object of a serious investigation at the Photographic Institution of the Royal Technical University in Stockholm. As a first result of this, two articles concerning the principal characteristics of the pressure effect were submitted to "Zeitschrift für Wissenschaftliche Photographie" in the autumn of 1943, but owing to the prevailing conditions they have not yet been published. For the sake of guidance we shall give some facts about the effect in question.

If the photographic material is subjected to pressure before or after the exposure no diminution of density is obtained after the development, which, however, is the case if the pressure is active while the exposure lasts. The greater the pressure is (we have used pressures up to 2000 kg. per cm^2), the greater is the effect. Generally sensitized materials (especially if they are sensitive to infra-red) show a greater pressure effect than unsensitized materials. The pressure effect also appears when a physical developer is used, which proves that the effect is founded in the latent image.

Hitherto nothing concerning the theory of the pressure effect has been published. We have, however, as has just been mentioned, definitely found that the effect is based in the latent image and not caused by varying rapidities of development for pressed and unpressed materials or other similar influences. Furthermore, it is a fact of the greatest importance that we only found the pressure effect associated with silver halide emulsions, i. e. with such photochemical systems, where the electrolytical conductivity plays a part in the photochemical process according to the theory of GURNEY and MOTT (4).

We further can distinguish a few different phases in the photochemical process, when silver halide emulsions are concerned. In the first place we have the primary light reaction, i. e. the absorption of the light quantum and the liberation of the electron from the halide ion. Secondly there are the movements of the electron and its ultimate capture by the sensitivity speck, whereby the latter becomes negatively charged. Thirdly we have the electrolytic conduction, i. e. the movement towards the speck of the vagabonding silver ions and their discharge there. A fourth factor, which affects the photochemical result, is the influence of the size of the speck upon its stability. Lastly there is the action of the development which is manifested in different effects.

Everything seems to indicate that the two first factors in the photochemical process generally cannot be affected by external influences. Instead we wish to explain the pressure effect as a diminution of the electrolytic conductivity of the silver bromide by the pressure. In order to check this hypothesis Mr. Arne Lundh at the Royal Technical University has carried out a series of experiments, still unpublished, concerning electrolytic conduction in silver chloride and bromide lamellae, subjected to static pressures of different magnitudes. He found that the conductivity was diminished by pressure. This is also proved by the work of Jost and Nehlep (9).

We have already pointed out that the first germ of a development nucleus, which is perhaps composed of only a few atoms, must be considered less stable than at a later stage. If consequently an electron, primarily liberated by light, has settled on the sensitivity speck, it may happen that it is again liberated owing to thermal agitation, in which case the positive silver ion may diffuse again (Webb and Evans, 5). This effect will naturally be of greater influence if the silver ions arrive sparsely one by one during the exposure either owing to a low light intensity (Webb and Evans, 5) or to a low electrolytic conductivity. The latter occurs if the material is either subjected to low temperature (Webb and Evans, 10) or, according to us, to heavy pressure.

In their work concerning the deviations from the law of reciprocity attending exposure at low light intensities, Webb

and Evans (5) have carried out a series of experiments where all the exposures were made with equal quantities of light, but in the different cases these were divided into two parts. Thus the photographical effects were compared when the first half of the exposure was carried out at very low light intensity and the second half at comparatively high ("optimum") intensity, and when the order was reversed. It is clear that in the first case the efficiency must be very low during the first half of the exposure, since the increase of the nucleus is greatly impeded by the simultaneous disintegration of the silver. Only during the second half of the exposure does the nucleus gain greater stability and then increases rapidly. If the exposures are carried out in the opposite order, the disintegration has no time to do any appreciable damage during the first exposure at high intensity, owing to the speed with which the nucleus increases; the second exposure (at low intensity) will therefore have an already stable nucleus as basis and its efficiency will be comparatively high. It is therefore obvious that after the development a greater density should be obtained in the second case than in the first. The experiments of Webb and Evans confirm this.

If our opinion is correct that by the application of pressure to photographic material the electrolytic conductivity is temporarily lowered, one ought to expect results analogous to those of Webb and Evans mentioned above when the exposure is carried out alternately with and without pressure. This matter will be investigated in the next section of this paper.

On the other hand one would expect the sensitivity specks to become more stable and the pressure effect to diminish, if the specks were increased before the exposure by intensification with mercury or silver. This will be examined in the following sections.

Some Intermittent Exposures Alternately With and Without Pressure.

The pressure apparatus for our experiments is illustrated in Fig. 1. In the lamp box (L) there is a motor-car lamp, the

light of which after reflection by the mirror (P) in the metal cylinder (C) reaches the solid glassplate (G). On this we place the film and against the latter a plug of steel (shown in the inset). The plug is pressed against the film by the lever (A), which rests against an edge (E) on the stand and is loaded at (D). In order to eliminate reflected light, diaphragms are mounted at X and Y, and between the film and the plug is placed a sheet of black paper. At (V) a colour-filter can be

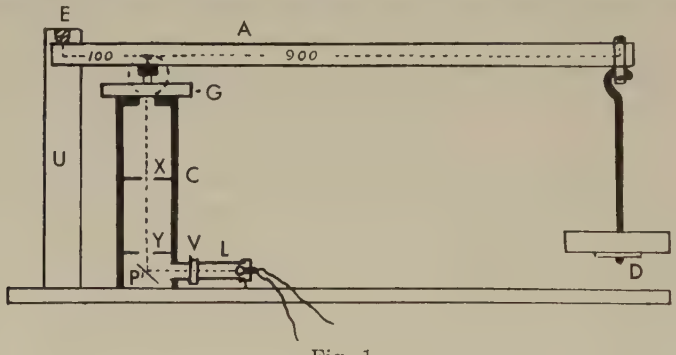

Fig. 1.

placed. In each exposure an inner circular area of 0.5 cm^2 is obtained, which has been exposed under pressure, and around it a ring with an outer diameter of 20 mm, which has been exposed without pressure but otherwise in the same way; after development the inner area always shows lower density than the outer one.

The experiments consisted in a number of exposures with identical intensities. Every exposure, however, was divided into two parts, one of which took place with pressure and the other without pressure. At first two series of experiments were made with *Agfa Infrarot 850 H*, as it had been apparent in our former work that infra-red sensitized material would show a high pressure effect. The light passed through a red filter (*Agfa 42*). The pressure was 1085 kg per cm^2. Then followed development for 5 minutes in an ordinary elon and hydroquinone developer.

The densities obtained were measured with an Eastman Transmission and Reflection Densitometer.

In Series I and II of the experiments the total duration of

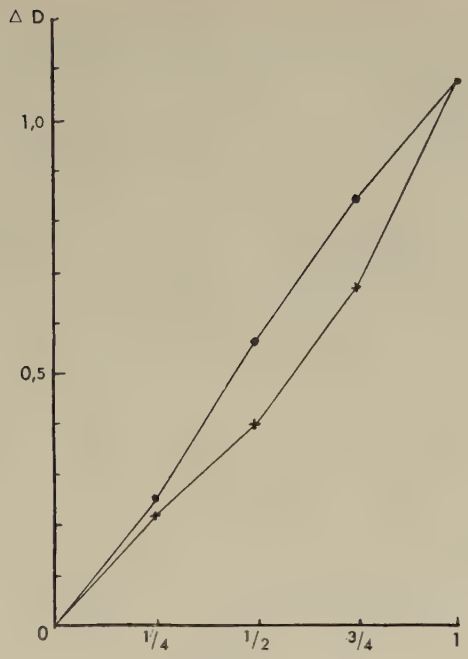

Fig. 2.

each exposure was 4 seconds. This period was, however, divided according to the following scheme:

4″	with	pressure	+ 0″	without	pressure
3″	»	»	+ 1″	»	»
2″	»	»	+ 2″	»	»
1″	»	»	+ 3″	»	»

Corresponding experiments were also made with the parts of the exposure in the opposite order.

The result of one of these Series (No. I) is shown in Fig. 2. The second is of the same type. On the abscissa axis we have marked out the fraction of the exposure carried out under pressure, while the pressure effect (the diminution of density △ D) has been taken as ordinate. The upper line represents exposures with pressure preceding those without pressure. The other line represents exposures made in the opposite order.

These series completely confirm our expectations. If the exposure with pressure precedes that without pressure a much greater diminution of density is obtained. This will indicate that the *first* part of the exposure *with pressure* does not stabilize the nuclei as much as that without pressure. The cause of this lies in the lower electrolytic conductivity, owing to which the silver ions need a longer time to reach the nuclei. The pressure effect is rather great, a maximum diminution in density 1.08 for a total density 3.18 in Series I and a maximum lowering 1.28 of a total density 2.37 in Series II.

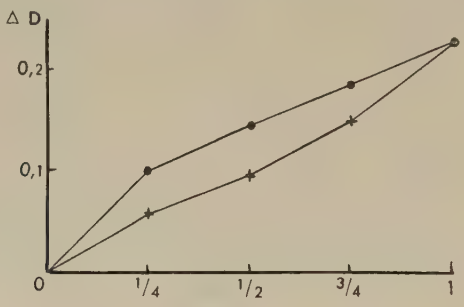

Fig. 3.

We have also made similar experiments with unsensitized bromide material (*Eastman Commercial Film*). As only small pressure effects might be expected with such material, the pressure was raised to 1885 kg per cm^2. Fig. 3 shows the result, which corresponds wholly to our expectations.

We have also carried out some series of experiments of a similar kind using an emulsion with silver chloride (*Ilford Contact Film*) instead of silver bromide as principal halide. The pressure was 1085 kg. per cm^2. The development times varied for three otherwise equal series from 40 seconds up to 10 minutes. The results of all the series were wholly like the previous ones.

Some Attempts to Stabilize the Nuclei Before Exposure by Means of a Mercury Intensification.

It has already been pointed out that a low light intensity or a heavy pressure during the exposure impairs the photochemical

result on account of the imperfect stability of the first nucleus germs. It is therefore reasonable to try to increase the nuclei with a metal, thus stabilizing them before the exposure. Under such circumstances one ought to obtain an improved photochemical result and a lower pressure effect.

As a means of intensification of the nuclei we first considered mercury vapour, Dersch and Dürr (11) having shown that if a photographic material is exposed to mercury vapour for a few days, an increased density is obtained after exposure and development. It seemed as if the sensitivity of the

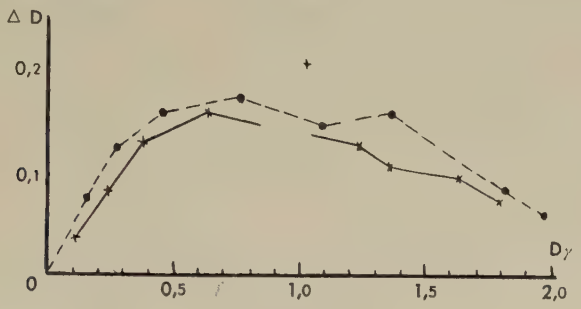

Fig. 4.

material had increased (generally by about 100 per cent). An explanation is that mercury is adsorbed by the small nuclei, possibly in the form of silver amalgam, whereby the nuclei increase in size. For this reason the light need not liberate as much silver as usual on the nucleus, in order to render the grain capable of development.

The difficulties are, however, several and in part rather important when this effect is to be used to test the influence on the pressure effect of the original size of the nucleus. First of all the sensitivity of the material is changed. This means that we come higher on the characteristic curve for an *equal exposure*. The absolute value of the pressure effect is, however, changed hereby. Generally it is a fact that with increasing exposure, i. e. with rising density values, the pressure effect will first rise to a maximum and then fall again. In accordance with the original position on the characteristic curve one ought to expect either an increase or a diminution of the pressure effect as a result of intensification of the

nuclei with mercury; for this reason it will be difficult to interpret the results of the experiments.

Recently Strock (12) has shown that the speed of the development is to a great extent dependent upon the light intensity with which the exposure is carried out. The difference is particularly obvious in the beginning of the development but is gradually levelled as the density approaches its final value. It is likely that the magnitude of the pressure, which in many ways has influences analogous to those of low light intensity, will also change the development speed in a similar

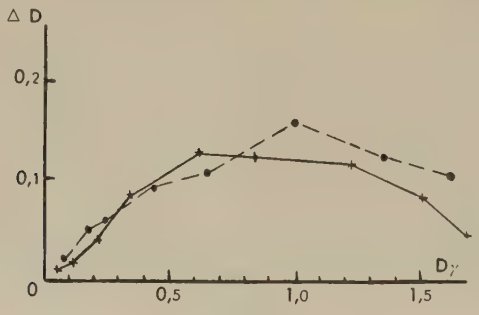

Fig. 5.

way. In order to eliminate this factor a comparatively long development time should be used in this investigation of the effect of mercury treatment on the pressure effect.

On the basis of these considerations we have arrived at the following experimental procedure. With the original silver bromide material as well as that treated with mercury a series of different exposures was carried out. For each of these a small circular area exposed with pressure and a surrounding area exposed without pressure were obtained. They were all developed in metol-hydroquinone for equal times, which had to be comparatively long. Afterwards the areas exposed without pressure, showing the *same* density, are selected from both series (that treated with mercury and the other). Evidently we have in these two cases the same number of developed grains per unit area which are naturally the grains that from the beginning had the largest nucleus germs. The important point is that the *same class of grains* is concerned in

each case. All the nuclei of the material treated with mercury should be larger than the corresponding nuclei of the untreated material. If we then compare the density diminution for the areas exposed with pressure that correspond to the areas with the same density exposed without pressure, the density diminution ought to be smaller for the material treated with mercury on account of the larger and more stable sensitivity specks of the latter. Unfortunately, however, one cannot expect a very large effect from this method, as we study the greatest grains in both cases the nuclei of

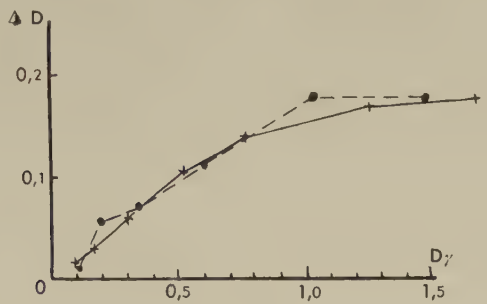

Fig. 6.

which ought in the beginning to have already reached a comparatively stable phase.

We have now made several series of experiments on the influence of mercury treatment, using different types of photographic material and different times of development.

The first series was made with an unsensitized bromide material (Fig. 4) *Agfa normal.* The film was treated with mercury vapour for 44.5 hours. The pressure during the exposure was 1885 kg per cm^2 and the development time was 2.5 minutes in the ordinary Elon-hydroquinone developer. In spite of the pressure effect being relatively small with a material of this kind and the development time comparatively short, the curves show a very characteristic course. Except for one single point the values of the pressure effect on the material treated with mercury (crosses in the figure) lie beneath the values of the untreated material (dots in the figure). This is consequently quite in line with our expectations from the theoretical point of view. The single divergent value must

be considered as a fortuitous error. — With a material sensitive to infra-red, *Agfa Infrarot 850 H*, and also with a panchromatic film, *Gevaert Ultra Panchro*, similar results were obtained.

We have also made a few series with a material also containing silver chloride, *Agfa Diapositiv Film*. We show three of these series in Figs. 5—7. For all these a pressure of 1085 kg per cm^2 was used but the development times varied: 1 1/4 minutes (Fig. 5), 2 1/2 minutes (Fig. 6) and 10 minutes (Fig. 7); for a material containing silver chloride the last development

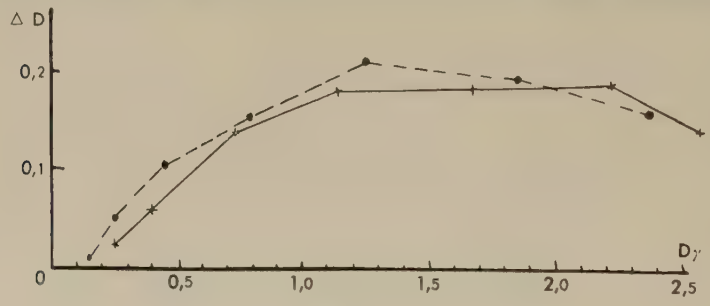

Fig. 7.

time must be considered very long. The durations of the mercury treatment were 5 days, 5 days and 11 days respectively. The latter factor however, will hardly affect the comparability of the results to any important degree on account of the fact that the sensitivity does not in general change much, if the treatment with mercury vapour is extended beyond a day or two.

If we now inspect the three figures, we observe on the whole the same effects, i. e. that the curve for the material treated with mercury lies lower than the other. At the two shortest development times, however, the differences between the curves are sometimes so small that they lie beneath the limit of error; a few deviations can therefore be observed. For the development time of 10 minutes the course is more pronounced and the curve for the material treated with mercury lies, for almost the whole of its length, beneath the other curve. This corresponds excellently to our theoretical expectations.

It may be added that we also carried out two other series with *Agfa Diapositiv Film* under the same circumstances but with development times shorter still (20 and 40 seconds respectively). In this case the curves for the pressure effect of the material treated with mercury as well as those of the untreated material coincided within the limits of experimental error.

To sum up the results given in this section we may state that they completely confirm the conclusions we drew from theoretical considerations. *In mercury treatment of the material we seem to have found a method of attacking a certain point in the photochemical mechanism of silver halide emulsions, i.e. the influence of the slight stability of the small primary nuclei. Even if this method does not seem to give extremely great effects, its suitability seems excellent with respect to checking the theory of the latent image.*

Some Attempts to Stabilize the Nuclei Before the Exposure by Means of Silver Intensification.

It is now quite reasonable to suggest an intensification of the nuclei by silver instead of mercury. Naturally this would in itself be better, as it would correspond better to the actual circumstances attending the increase of the nuclei in the normal photographic process. In reality, however, the silver intensification of the nuclei would involve certain complications, as it must be made with an intensification bath which might affect the material in other respects too, the bath containing several different chemicals of which some must be considered very "vigorous". The merit of the mercury method lies above all in the fact that it leaves the material unchanged otherwise since the intensification takes place while the emulsion is *dry*.

We have, however, made a few introductory experiments with silver intensification employing the following physical developer:

Solution A:

Distilled water	500 ml
Sodium sulphite cryst.	45 g.
Silver nitrate 10 % sol.	35 ml

Solution B:

Distilled water	500 ml
Sodium sulphite cryst.	10 g.
Hydroquinone	3 g.

For use, equal parts of the two solutions were mixed. The temperature of the bath should be 20° C.

In this bath silver nitrate is reduced to silver. First a colloidal solution of this is obtained and from this silver is precipitated on to the specks in the photographic material, whereby these ought to increase in size and thus also in stability.

One may, however, expect the water to dissolve potassium bromide of which there remains an excess in the material after the manufacture. As the percentage of potassium bromide is of great importance with respect to the sensitivity of the material, it is necessary that the material for comparation should be placed into a water-bath, preferably for as long a time as that treated with silver.

We only performed a couple of series with this type of treatment. The pressure was 310 kg per cm^2. In order to avoid complications from the influence of the intensification solution on the sensitizing dyes, we used an unsensitized material, which, however, had the disadvantage of a rather low pressure effect. The development took 3 minutes in Elon-hydroquinone.

The result of the first experiment is shown in Fig. 8. It is not very convincing, and the experiment certainly ought to be repeated with the use of greater pressure and a longer development time. For the lower densities up to 1.5, however, it shows the course that we foretold. Thus the pressure effect is smaller for the material intensified with silver than for the original one. On the other hand the circumstances are the opposite at densities over 1.5. The cause of this is difficult

to determine. A second series of experiments, carried out under similar circumstances, shows quite analogous results.

Naturally it may be said that the first part of the curve at low or medium densities is the most important and that the chances of complications henceforth become greater. The experiments can therefore to a certain extent be said to confirm our opinion, although not so strongly as would be desirable. On the other hand it is obvious that the "wet" method with silver intensification is not so sure as the "dry" one with mercury vapour.

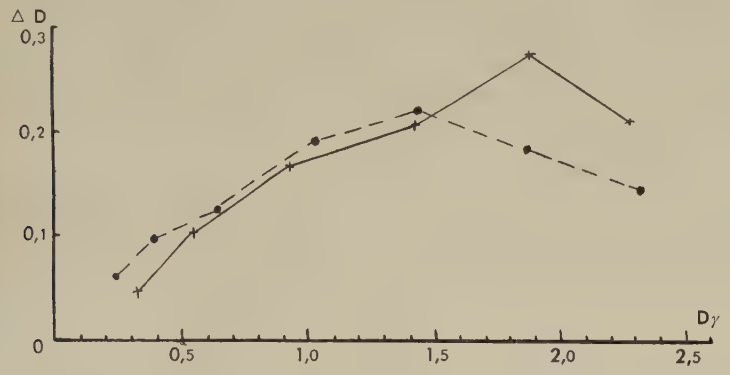

Fig. 8.

It seems probable that a method should also be applicable opposite to that used in the mercury and silver intensification, i. e. to decrease the existing sensitivity specks, for instance by means of chromic acid. Subsequently we intend to try this method also. As a "wet" method is concerned, it might not be wholly free from complications; but at any rate these ought not to be greater but rather smaller than those of the silver intensification method.

Discussion.

Gurney and Mott (4) have recently given a complete theory for the mechanism of the photochemical process in photographic material (silver bromide or silver chloride in gelatine). This theory is capable of explaining the different photographic

effects from a single viewpoint. According to this theory a series of different phases can be distinguished when the latent image is formed (p. 68). Under such circumstances it is possible to affect one phase at the time of the photochemical reaction by special treatments, and great possibilities are thus revealed for checking the theoretical conclusions. Thus Webb and Evans (10) have been able to affect the electrolytic conductivity by means of a change in the temperature of the experiment, owing to the fact that the conductivity can be greatly diminished at a low temperature. In our opinion a great pressure on the emulsion during exposure also results in a diminution of the electrolytic conductivity, and therefore in the same way will influence the mechanism forming the latent image. On the whole the effect is the same as if a lower light intensity is used at the exposure. We have given some experimental proofs of this.

On the other hand, according to what has been shown here, it is possible to affect the stability of the nuclear germs either by increasing them with a metal (mercury or silver) or possibly by reducing them. We have particularly investigated the first case by mercury intensification according to the "dry" method, and the results obtained have confirmed our theoretical deductions. When using the silver method, the intensification is made in the "wet" way, and this will more easily give rise to complications. Our experiments, however, seem to indicate that the method is not quite hopeless. Nevertheless it must be subjected to further investigations. This also applies to the last mentioned reducing method.

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A Self-Registering Apparatus for Adsorption Analysis.

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During recent years the development of adsorption analysis and its applications to various important problems have been studied intensively by Tiselius and his collaborators at Uppsala (1—10). The experimental arrangements have, of course, been improved or changed at intervals. Earlier a description of a microinterferometric system has been published by Tiselius and the author (7). In this case the refractive index and the volume of a solution which had just passed a filter containing a suitable adsorbent were determined at very short intervals. By plotting the refractive index as a function of the volume, characteristic curves were obtained from which the composition of the solution could be calculated. This method, however, had the great disadvantage that readings had to be made incessantly and often for many hours. The need of a self-registering apparatus, especially for experiments lasting for days, was therefore acute. This paper gives a description of such an apparatus, built during the past year.

The construction of a self-registering apparatus for the purpose mentioned really involves two problems, namely the registering of the refractive index and that of the volume or weight of the solution with accuracies of 10^{-5} and 0.1 ml respectively. These two registering arrangements should then be co-ordinated so as to give only one curve on a photographic paper.

The registering of the refractive index was arranged in the following manner (see Fig. 1). The solution, after having passed the adsorbent, enters one of the halves of a double prism (D). The other half is filled with solvent. The angle between the

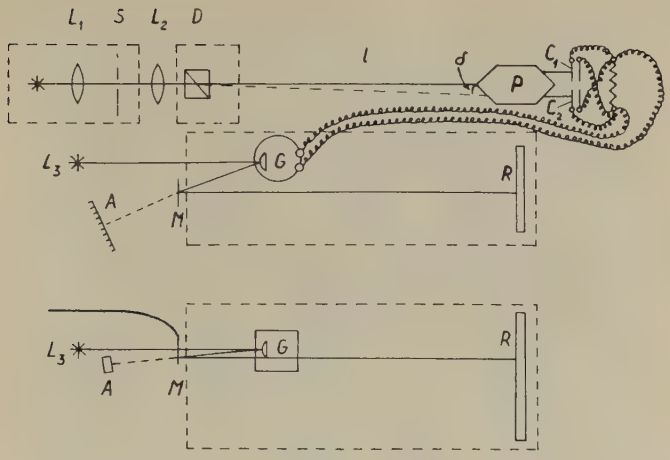

Fig. 1. Sketch of the apparatus

halves is 45°. A beam of light from the slit (S) travels through the prism and falls on the edge of a hexagonal prism (P) of glass, where it is split into two parts, each falling on a blocking-layer photo-element, (C_1) and (C_2). The two elements are connected with a galvanometer (G) in such a way that no current passes through it when the elements are equally illuminated.

We now suppose that the refractive index of the solution in one of the halves (D) changes by $\Delta\mu$, causing the light beam to move a distance δ. The following relation holds

$$\Delta\mu = \frac{\delta}{l} \tag{1}$$

where l is the distance between the prisms. The movement of the light beam gives rise to unequal illumination of the elements (C_1) and (C_2) and the galvanometer makes a deflection which can be registered on the photographic paper (R).

In the expressions for the amount of light F which moves from one of the elements to the other when the light beam moves through δ following the change $\Delta\mu$ in the refractive index, we use the following notation: the galvanometer deflection n, the illuminating power of the lamp L, the current from the photo-cells I (which is assumed to be proportinal to

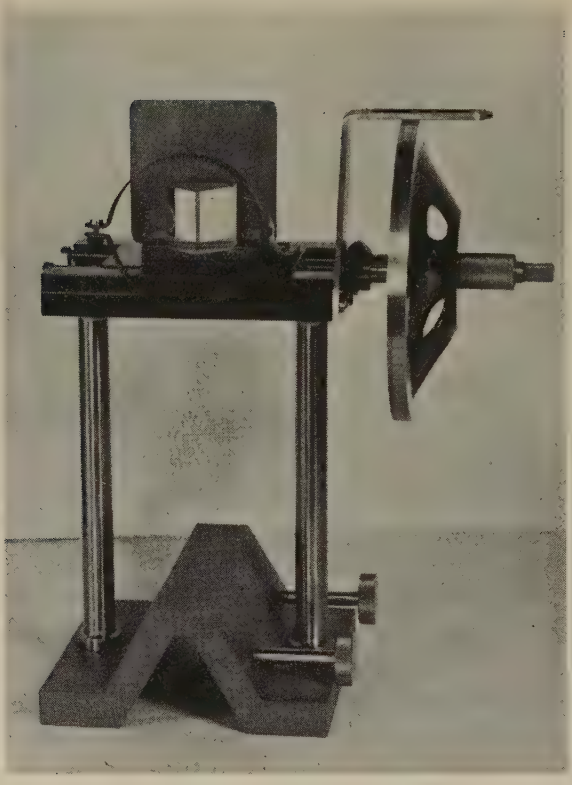

Fig. 2. The slide with the hexagonal prism.

the amount of light F); k, k_1, k_2 and $K = k \cdot k_1 \cdot k_2$ are constants. We then have

$$\begin{aligned} F &= k \cdot L \cdot \delta \\ I &= k_1 \cdot F \\ n &= k_2 \cdot I \\ \therefore n &= k\, k_1\, k_2 \cdot L \cdot \delta = K \cdot L \cdot \delta \end{aligned} \tag{2}$$

and from (1) we have

$$n = K \cdot L \cdot l \cdot \Delta\mu$$

or

$$\Delta\mu = \frac{1}{l} \cdot \frac{1}{K \cdot L} \cdot n. \tag{3}$$

From (3) it is found that $\Delta\mu$ is directly proportional to the galvanometer deflection n if the photo-elements have linear

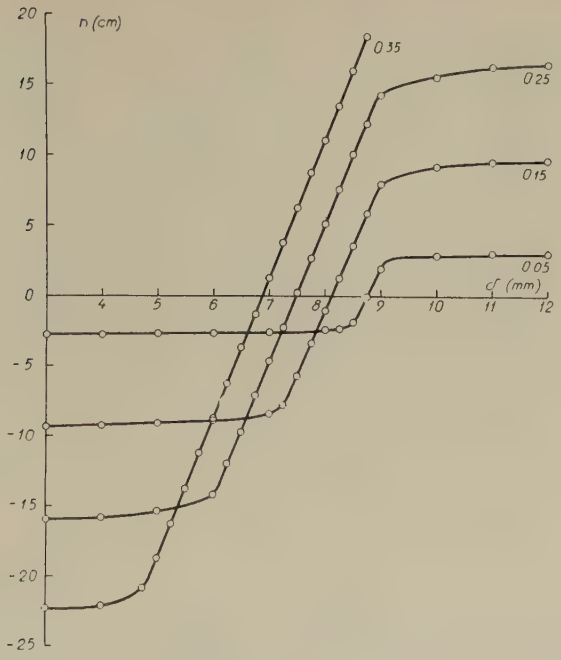

Fig. 3. The galvanometer deflection n as a function of the distance δ for different widths of the slit.

characteristics (i. e. if k_1 is an absolute constant). It is also seen from (1) that if l is chosen as 1 000 mm and $\Delta\mu$ as 10^{-5} the relation gives $\delta = 0.01$ mm, and in order to make the galvanometer deflection 1 mm the amplifying factor KL must have the value of 100. These two requirements may be satisfied by blocking-layer photo-elements if the prescriptions concerning their coupling given by Wood (11) are observed. As photo-element a "Differenzial Photoelement S 60" from B. Lange has been employed. The galvanometer was a "Moll Original" type D (resistance 65 Ω and sensibility $2.4 \cdot 10^{-9}$ amp./mm.). The galvanometer was shunted by a 35 Ω resistance.

The prism (P) and the elements (C_1) and (C_2) are mounted on a slide that may be moved at right angles to the light beam by means of a micrometer screw, which can be read to 0.001 mm (see Fig. 2). Equation (2) was used in showing that the galvanometer deflections are directly proportional to the difference in the light-intensities between the elements (C_1) and (C_2).

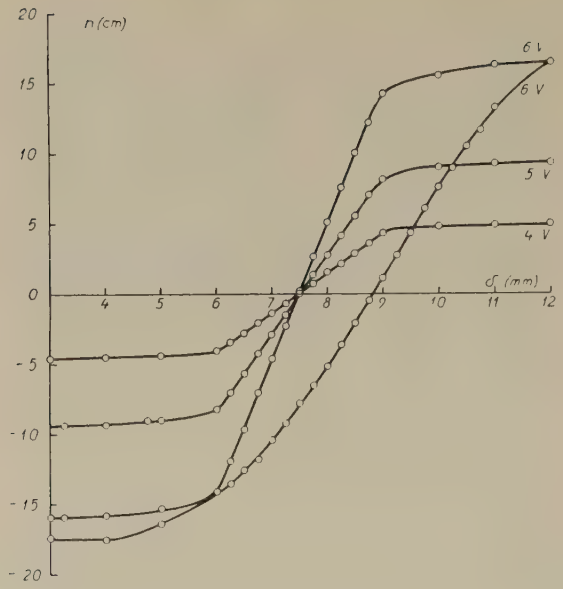

Fig. 4. The galvanometer deflection as a function of the distance δ for different lamp-voltages.

To give δ different values the slide was moved by the micrometer screw. The corresponding galvanometer deflections were observed and the results are given in Figs. 3 and 4, which show the complete linearity. Furthermore, it is seen that $K \cdot L$ is independent of the width of the slit but depends on the light-intensity (voltage of the lamp). The values of Table 1 are taken from Fig. 4.

Table 1.

Voltage (volts)	$K\,L$
6	97
5	56
4	28

It is evident that the sensitivity of the apparatus can be varied over a wide range.

The author decided to weigh the solution that had passed

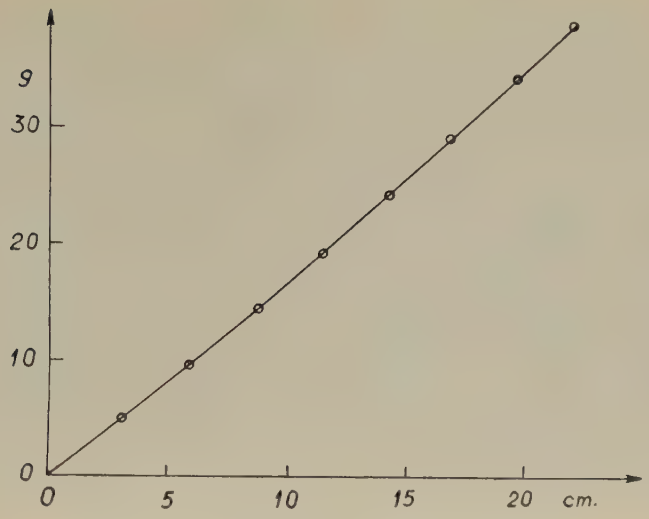

Fig. 5. Calibration curve for the spring.

through the double prism instead of measuring its volume. The choice of the balance was of great importance, as very different amounts of solutions are used in different experiments (from 10 g to 1 000 g), and so the balance must be easy to replace by others with different sensitivities. Simple straight springs seem to be best suited. The spring is fastened horizontally at one end, while at the other hangs a vessel into which the solution drops. The balance is damped by a small metal plate dipping into paraffin oil. For the loaded spring the well-known formula

$$\tan \alpha = \text{constant} \cdot P$$

holds, where α is the angle between the free end and the horizontal plane and P is the load. At the free end of the spring a mirror is fastened, the deflection being registered as usual by means of a light spot on a scale. As the arc tan correction does not enter, the deflection is directly proportional to the load. A typical calibration curve is shown in Fig. 5. The curves have not changed during six months.

The registering devices for refractive index ($\Delta\mu$) and weight (g) are co-ordinated in the usual way with crossed mirrors and thus $\Delta\mu$ is registered as a function of g. The mirror on the

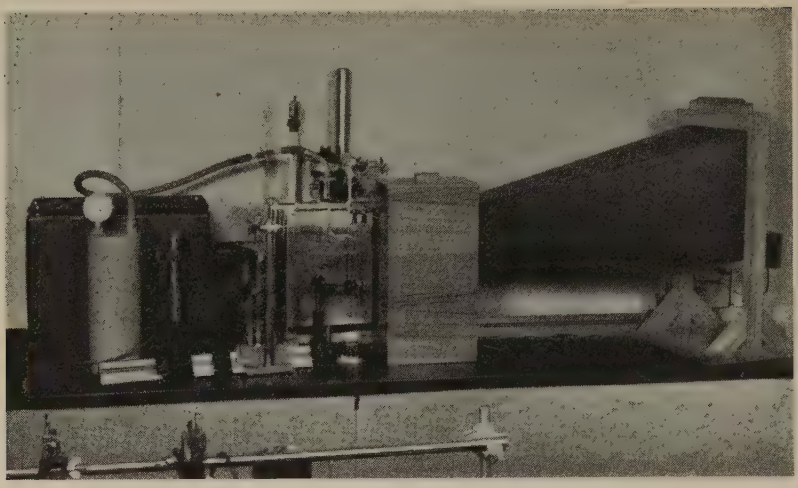

Fig. 6. Photograph of the complete apparatus.

balance moves at right angles to the galvanometer mirror (see Fig. 1). A narrow beam of light from the illuminating device (L_3) first reaches the galvanometer mirror and then the balance mirror (M) and forms a point image on the photographic paper (R). When the refractive index changes the image moves horizontally and when the weight increases it moves vertically, and so it describes a curve of the type desired with $\Delta\mu$ as a function of g. The photographic paper has a size 21 × 29 cm (DIN A 4). The whole apparatus and registering devices are surrounded by lightproof housings. The apparatus may even be used in broad daylight. To render it possible to observe how the experiments proceed, the mirror (M) is half-reflecting and an image falls on the scale (A). The double prism (D) is immersed in a thermostat. Fig. 6 is a photograph of the complete apparatus.[1]

The construction of the double prism is seen in Fig. 7. The filter for the adsorbent and the other arrangements are the same as in the earlier apparatus (6, 7) but here much larger filters can be used with volumes of 400 cm^3.

The volume in the double prism available for the solution is 0.23 ml, which is small enough to avoid considerable "volume-lag".

[1] The complete apparatus is now manufactured by *LKB Produkter Fabriks AB*, Alvik, Stockholm.

Fig. 7. The double prism in parts.

In order to get an expression of the "volume-lag" the following calculation is made. Suppose that complete mixing in the volume a (= 0.23 ml) occurs, which is the most unfavourable case. The concentration of the solution moving into the apparatus has the value $c_0(v)$, that in the apparatus $c(v)$. If now a small volume dv with the concentration $c_0(v)$ enters, the concentration in the volume a increases by dc and at the same time a volume dv with the concentration $c(v)$ leaves. Then we have as a measure of the increase of substance in the volume a

$$a \cdot dc = c_0(v)\,dv - c(v)\,dv$$

or

$$\frac{dc}{dv} + \frac{c(v)}{a} = \frac{c_0(v)}{a}$$

with the solution

$$c(v) = e^{-\frac{v}{a}} \left(\text{const.} + \int_{v_0}^{v} e^{\frac{v}{a}} \cdot \frac{c_0(v)}{a}\,dv \right). \qquad (4)$$

In Fig. 8 two typical curves have been drawn according to (4). The dotted line gives the real values of $c_0(v)$, the heavy line gives the observed $c(v)$. The deviation is obviously so small and of such a nature that it may be neglected.

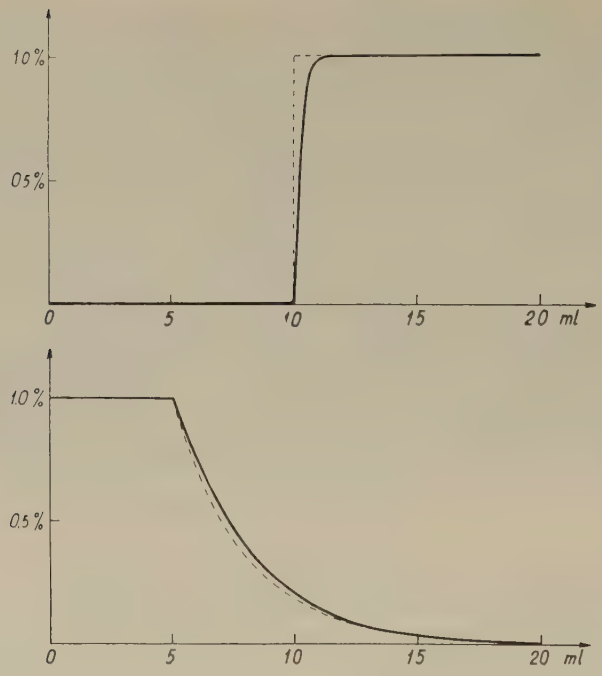

Fig. 8. Illustration of the "volume-lag".

Before the apparatus is fit for use it must of course be calibrated, i. e. the proportional constant $\frac{1}{l} \cdot \frac{1}{KL}$ in equation (3) must be determined. The first factor $\frac{1}{l}$ is a non-changing apparatus constant, the second $\frac{1}{KL}$ is the photoelectric amplification factor which is subject to certain variations, e. g. decreasing sensitivity of the photo-elements. On account of this $\frac{1}{KL}$ is determined at the beginning of each experiment, $\frac{1}{l}$, however, is measured once and for all in the following way. First the double prism (D) is filled with redistilled water and the prism (P) moved until no current passes through the galvanometer, zero deflection. Then the apparatus is filled with a solution of known refractive index and the prism (P) moved again to zero galvanometer deflection. The distance δ is read

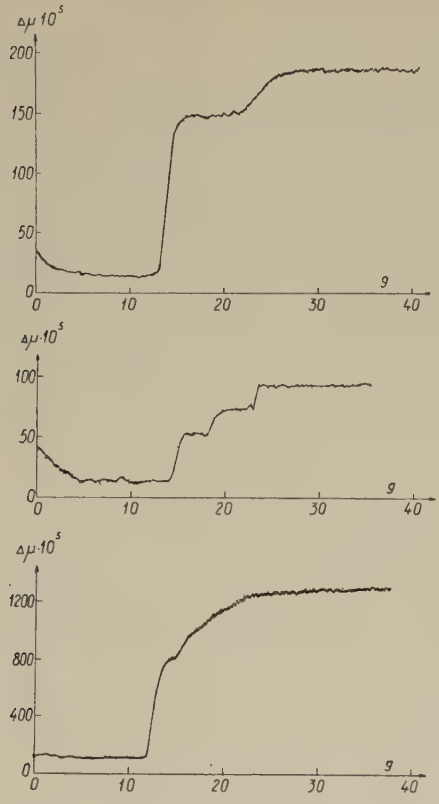

Fig. 9. Front analysis of fatty acids, filter containing about 4 g active carbon "E-kol".

a) 0.75 % lauric acid + 0.75 % palmitic acid
b) 0.3 % lauric + 0.3 % myristic + 0.3 % palmitic acid
c) 3 % capronic + 3 % myristic + 3 % palmitic acid (incompletely separated).

on the micrometer screw and $\frac{1}{l}$ is calculated from (1). As standard solutions sodium sulphate and lithium chloride are used, their refractive indices being taken from tables (12) (13). The results are giving in Table 2.

KL is determined in the following way: the prism (P) is moved 1 mm by the micrometer screw, the corresponding galvanometer deflection n (in mm) gives KL directly according to (2). Its value is about 100 at the highest sensitivity (see

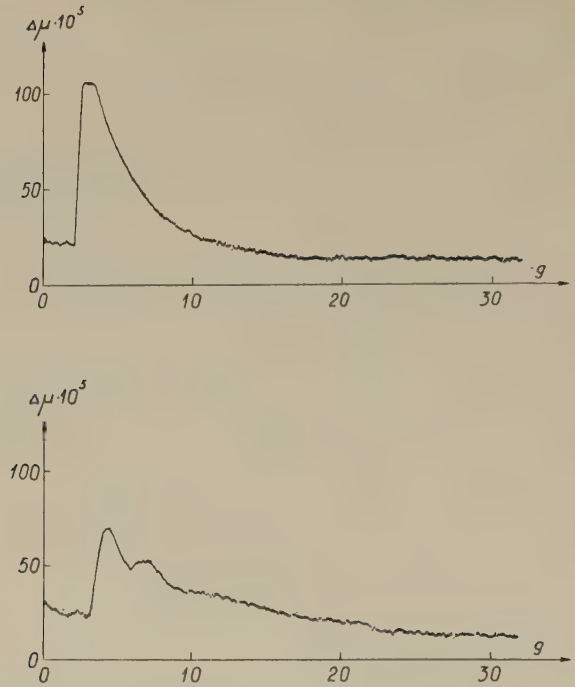

Fig. 10. Elution analysis of fatty acids, filter containing 1.6 g carboraffin C. a) 35 mg palmitic acid b) 20 mg capronic acid + 30 mg palmitic acid.

Table 2.

Na_2SO_4		$\lambda = 589$ mμ	Temp. 25.0°C
Conc.	$\Delta\mu \cdot 10^4$	δ (mm)	$\frac{1}{l} \cdot 10^3$
0.8872 N	88.21	12.765 — 3.694 = 9.071	0.972
1.0448 N	102.72	14.276 — 3.692 = 10.584	0.971
1.1705 N	114.09	15.462 — 3.695 = 11.767	0.975
1.3399 N	129.18	16.989 — 3.688 = 13.301	0.972
Li Cl		$\lambda = 546$ mμ	Temp. 20.0°C
Conc.	$\Delta\mu \cdot 10^4$	δ (mm)	$\frac{1}{l} \cdot 10^3$
0.2312 N	21.21	8.928 — 6.746 = 2.182	0.974

As mean value we obtain $\frac{1}{l} = 0.973 \cdot 10^{-3}$.

Table 1). That makes $\frac{1}{l} \cdot \frac{1}{KL} = 10^{-5}$, i. e. 1 mm on the diagram corresponds to $\Delta\mu = 10^{-5}$.

Fig. 9 and 10 show some typical diagrams. All the curves represent solutions of fatty acids in ethyl alcohol and are obviously rather satisfactory.

The same method for registering refractive indices can naturally be applied to various other problems where it is important to make continuous observations of changes in concentration. Destillation, titration and extraction may be mentioned in this connection. If convenient, the photo-elements may be replaced by other light-sensitive devices, for instance vacuum photo-cells or thermo-elements.

Summary.

A self-registering apparatus for adsorption analysis has been described. It gives refractive index as a function of the weight of solution that has passed through it. The accuracy is about 10^{-5} and 0.03 g respectively at maximum sensitivity. The apparatus is well adapted also to problems other than adsorption analysis.

The author is deeply indebted to Professor Arne Tiselius for his kind interest in the work and for helpful criticism.

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Über die Grösse von Flüssigkeitsmenisken.

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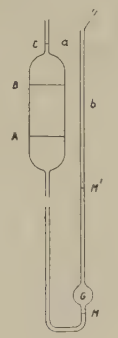
Bei einer Untersuchung über die Grösse der Korrektion, welche an kapillarviskosimetrischen Messungen für den Einfluss der Oberflächenspannung anzubringen ist, machte sich die Bestimmung der Meniskusvolumina von völlig benetzenden Flüssigkeiten in kreiscylindrischen Rohren nötig. Derartige Messungen liegen für Wasser bereits vor, dagegen nicht für Flüssigkeiten mit anderen Werten von Oberflächenspannung und Dichte, d. h. anderen Kapillarkonstanten. Es wurden deshalb solche Bestimmungen an einigen geeignet gewählten Stoffen vorgenommen. Die Resultate geben einerseits Aufschluss über die an Volumen und Druckhöhe einer Flüssigkeitssäule anzubringenden Korrekturen, andrerseits besitzen sie ein gewisses Interesse deshalb, weil gerade für das hier untersuchte Grössengebiet eine Vorausberechnung auf Grund exakter kapillartheoretischer Formeln bis jetzt noch nicht möglich ist.

Zu Grunde gelegt wurde die sehr sorgfältig durchgeführte und wohl alle praktisch in Frage kommenden Rohrradien umfassende Serie (zwischen 1 und 12,5 mm), welche Winkler (1) an Wasser bei 20° aufgenommen hat. Nachdem an sechs Glasrohren mit Radien zwischen 2,5 und 7,5 mm die Unterschiede der Meniskusvolumina der gewählten Substanzen gegen die des Wassers festgestellt worden waren, konnten diese Volumina selbst mit Hilfe von Winklers Werten leicht berechnet werden.

Die Glasrohre (vgl. Fig. 1) wurden mit kapillaren Ansätzen und feinen aufgeätzten Ringmarken (A, B, C) versehen. Nach Ermittlung des Rohrradius aus dem Abstande zwischen den Marken A und B und dem zwischen diesen enthaltenen Vo-

lumen wurde jedes Rohr (*a*) in der aus der Figur ersichtlichen Weise mit einem kleinen Hilfsteile zusammengeblasen, dessen rechte Seite (*b*) aus einem engen kalibrierten Rohr und einer Erweiterung (*G*) bestand. Diese fasste immer etwas weniger als das zwischen den Marken *B* und *C* enthaltene Volumen Wasser. Liess man dieses Volumen von (*a*) nach (*b*) übertreten, so nahm es dort eine Strecke *MM'* ein, die an einer Millimeterskala abgelesen wurde. Bei jeder anderen Flüssigkeit hatte *MM'* eine andere Länge, und der Unterschied gegen Wasser, auf Volumen umgerechnet, gab an, um wieviel Kubikmillimeter das jeweilige Meniskusvolumen kleiner war als das von Wasser. Die Versuchstemperatur betrug 25,0°.



Figur 1. Apparat zur Bestimmung von Meniskusvolumendifferenzen. *A*, *B*, *C*, Ringmarken.

Diese Werte in Verbindung mit den zugehörigen absoluten Wasserwerten nach Winkler ergaben die Meniskusvolumina selbst.[1]

Untersucht wurden 1. eine wässrige Lösung von Dichloressigsäure mit 6,28 % Säure (weiterhin bezeichnet mit *D*), 2. o-Xylol (*X*) und 3. Äthylenbromid (*Ä*). Die zugehörige Kapillarkonstante von *Ä* beträgt nach der Litteratur 3,51 mm^2; für *D* und *X* wurde mittels der Steighöhenmethode 10,82 resp. 6,90 gefunden, während die Kapillarkonstante des Wassers bei 25° $a^2 = 14{,}68$ mm^2 ist.

Die Messfehler der gefundenen Volumendifferenzen können zu etwa δ mm^3 geschätzt werden, wie in Tabelle 1 angegeben. Hierzu kommt der Fehler der Rohrradiusbestimmung, welcher 0,02 mm nicht übersteigen dürfte, sowie bezüglich der absoluten

[1] Der Einfluss des Temperaturunterschiedes von 5° wurde wegen der geringen Veränderlichkeit von a^2 bei Wasser vernachlässigt.

Beträge noch der Fehler von Winklers Bestimmung. Tabelle 1 enthält die Rohrradien R (in mm), die gefundenen Differenzen gegen Wasser (in mm^3) und unter v_w die zugehörigen Meniskusvolumina des Wassers.

Tabelle 1.

R	v_w	D	X	A	δ
2,51	12,9	0,9	2,8	4,1	$\pm 0{,}1$
3,45	29,5	1,9	5,9	9,0	0,1
4,25	50,8	3,1	10,8	23,0	0,1
5,06	80,0	8,8	23,8	42,0	0,2
6,27	136	13,7	44,7	81,2	0,3
7,52	201	23,8	81,2	129	0,4

Demnach beträgt z. B. für Äthylenbromid im Rohr mit $R = 7{,}52$ mm das Meniskusvolumen $v = 201 - 129 = 72$ mm^3.

Graphische Interpolation dieser Werte würde somit die Volumina v und die »reduzierten» oder »mittleren» Höhen $\mu = v/\pi R^2$ der Menisken für jede benetzende Flüssigkeit von bekannter Kapillarkonstante a^2 und jeden Radius zwischen 2,5 und 7,5 mm ergeben. An Stelle einer derartigen Tabelle sei hier eine Formel mitgeteilt, welche den Verlauf der gemessenen Werte von μ als Funktion von R in praktisch ausreichender Weise, d. h. auf einige Prozent genau, darstellt und zwar empirischer Art ist, aber insofern eine gewisse theoretische Grundlage zu haben scheint, als sie keinerlei willkürlich zu wählende Konstante enthält. Sie wird hier ihrer Einfachheit wegen sowie deshalb mitgeteilt, weil bekanntlich die Integration der theoretisch strengen Differentialgleichung des Meniskusvertikalschnittes bisher zwar mit Hilfe von Näherungsannahmen für sehr grosse Radien gelungen ist — (s. Litteraturübersicht unter 2), dagegen noch nicht für mittelgrosse, wie sie hier untersucht worden sind. (Die Theorie kann natürlich nicht voraussagen, wann ein Radius als sehr gross betrachtet werden darf).

Eine exakte Aussage lässt sich nur für die beiden Grenzfälle machen, dass R entweder gleich Null oder unendlich gross

ist. Im ersten Falle nimmt der Meniskus die Gestalt einer Halbkugel an, so dass

$$\mu = \frac{R}{3} = 0 \text{ und } v = \pi \frac{R^3}{3} = 0 \tag{1}$$

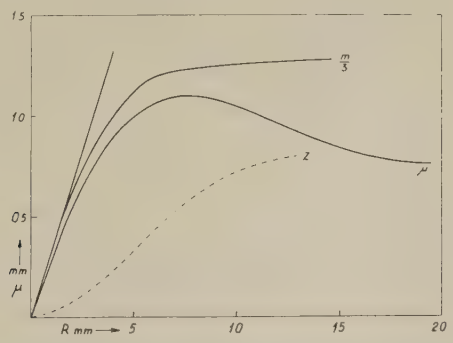
im zweiten nähert sich v dem gesamten durch die Oberflächenspannung gehobenen Volumen V, welches in jedem Falle durch Kapillarkonstante und Radius als $V = \pi \cdot a^2 \cdot R$ gegeben ist. Für $R = \infty$ wird dann

$$v = V = 0 \text{ und } \mu = \frac{a^2}{R} = 0. \tag{2}$$

Ferner variiert das »relative» Volumen des Meniskus, $z = v/V$, von $z = 0$ für $R = 0$ bis $z = 1$ für $R = \infty$, und die Höhe der Randlinie des Meniskus über dessen tiefstem Punkte beginnt mit $m = R$ für $R = 0$, um dann asymptotisch bis zum Grenzwerte $m = a$ für $R = \infty$ anzusteigen.

Die uns hier hauptsächlich interessierende Grösse μ steigt ebenfalls von Null an mit endlicher aber ständig abnehmender Tangente, sinkt jedoch im Gegensatze zu m schliesslich wieder gegen Null ab, und zwar asymptotisch; sie muss also bei endlichen Werten von R ein Maximum und nachher einen Wendepunkt durchlaufen.

In Fig. 2 ist der Verlauf von μ und z nach Winkler (1) sowie der von m nach Verschaffelt und van der Noot (3), ebenfalls für Wasser, dargestellt.



Figur 2. Mittlere Höhe μ des Meniskus und $^1/_3$ der Randlinienhöhe m sowie relatives Meniskusvolumen z in Abhängigkeit vom Radius. Links gemeinsame Grenztangente für μ und $m/3$.

Die erwähnte Formel, welche μ als Funktion des Radius in Verbindung mit der Kapillarkonstante a^2 ausdrückt, lautet

$$\mu = \frac{R}{3} \cdot e^{\frac{\mu - R}{2a}}. \tag{3}$$

Da stets $\mu < R$, so ergibt sie $\mu = 0$ sowohl für $R = 0$ wie für $R = \infty$. Als Bedingung für das Maximum liefert sie

$$0 = \frac{d\mu}{dR} = \frac{\mu}{\mu - a} \cdot \left(1 - \frac{2a}{R}\right) \tag{4}$$

d. h.

$$R_{\max} = 2a. \tag{5}$$

Die Wendepunktsbedingung

$$\frac{d^2\mu}{dR^2} = 0 \tag{6}$$

führt auf eine quadratische Endgleichung

$$(2a - \mu)^2 = (2a - R)^2 \tag{7}$$

mit den beiden Wurzeln

$$\mu_w = R_w \text{ und } \mu_w + R_w = 4a. \tag{8}$$

Die Kurve hat also zwei Wendepunkte; der erste fällt in den Nullpunkt, der andere wie zu erwarten jenseits des Maximums. Durch Kombination der Formeln (3) und (8) lassen sich Abscisse und Ordinate für jedes vorgelegte a ausrechnen

Die ausführlichste quantitative Prüfung gestattet die Wasserserie von Winkler. In Tabelle 2 finden sich ausser R die auf runde Werte des Radius interpolierten Höhen μ_f sowie die nach (3) berechneten μ_b. Die Übereinstimmung darf wohl als gut bezeichnet werden.

Die Höhen μ_f für die drei hier neu gemessenen Flüssigkeiten, welche sich aus den graphisch ausgeglichenen Volumengrössen der Tabelle 1 ableiten lassen, sind in Tabelle 3 den nach Formel (3) mittels der oben angegebenen Kapillarkonstanten berechneten unter μ_b gegenübergestellt. Auch hier ist die Übereinstimmung gut.

Tabelle 2.

R	μ_f	μ_b	R	μ_f	μ_b
2	0,56	0,55	8	1,13	1,10
3	0,73	0,74	9	1,11	1,08
4	0,86	0,89	10	1,08	1,05
5	0,99	1,00	11	1,03	1,01
6	1,08	1,06	12	0,97	0,97
7	1,12	1,09	12,5	0,94	0,94

Tabelle 3.

R	D		X		$\ddot{A}$	
	μ_f	μ_b	μ_f	μ_b	μ_f	μ_b
2,51	0,61	0,62	0,55	0,57	0,45	0,48
3,45	0,75	0,76	0,65	0,67	0,55	0,53
4,25	0,84	0,84	0,71	0,72	0,53	0,52
5,06	0,90	0,89	0,73	0,74	0,49	0,50
6,27	0,97	0,94	0,73	0,72	0,44	0,44
7,52	0,96	0,92	0,67	0,67	0,39	0,38

Am besten übersieht man die Verhältnisse in dem Diagramm Figur 3. Die Kurve ist nach Formel (3) berechnet, die eingezeichneten Punkte stellen Winklers direkt gefundene, nicht ausgeglichene Versuchsdaten dar. Ferner sind die berechneten Ordinaten für Maximum und Wendepunkt eingezeichnet, und endlich findet sich noch ganz rechts ein weiteres Versuchsergebnis, welches von Richards und Carver (4) auf anderem Wege an Wasser gewonnen wurde. [Über die gestrichelte Kurve s. u. S. 102].

Diese Autoren bestimmten den Krümmungsradius im Centrum eines Rohrs von 19,4 mm Radius mittels Reflexionsbeobachtungen zu etwa 0,9 Meter, woraus folgt, dass diese Stelle um 0,016 mm über dem Nullniveau liegt. Dem entspricht ein Volumen des cylindrischen Teiles der gehobenen Säule von $\pi \cdot 19{,}4^2 \cdot 0{,}016 = 19$ mm^3, und da sich das gesamte gehobene Volumen zu $V = 906$ mm^3 berechnet, so ist $v = 887$ mm^3 und

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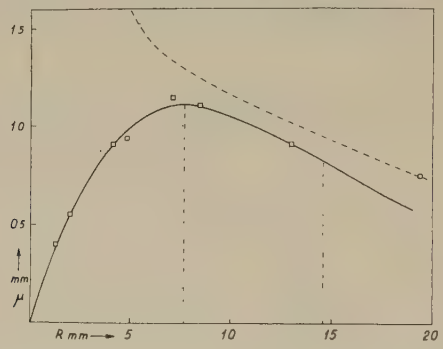
$\mu = 0{,}75$ mm. (z liegt hier mit 0,98 schon dicht am Grenzwerte $z = 1$).

Die Längen der Maximalordinaten für alle vier Flüssigkeiten ergeben sich aus den Versuchen zu 1,11 (Wasser), 0,97 (D), 0,75 (X) und 0,57 ($\ddot{A}$), während sie nach der Berechnung 1,09, 0,95, 0,74 und 0,53 betragen sollen. Diese berechneten Punkte bilden eine Gerade mit der Neigung $\mu : 2a = 0{,}141$ gegen die Abscissenaxe.

Die Wendepunkte für D und X fallen nicht innerhalb des



Figur 3. Berechnete und gefundene Meniskushöhen für Wasser. ——— berechnet nach Gl. 3, – – – – berechnet nach Verschaffelt, □ gefunden von Winkler, ○ gefunden von Richards und Carver. — — — — Ordinaten für Maximum und Wendepunkt.

gemessenen Gebietes, der für $\ddot{A}$ berechnete scheint mit der gefundenen Kurve verträglich zu sein.

Versuchsweise sei noch Formel (3) auf eine überhaupt nicht benetzende Flüssigkeit angewendet. Bei einer solchen liegen die Verhältnisse genau umgekehrt wie bei den völlig benetzenden Stoffen, und als Meniskusvolumen ist das cylindrische Komplement der Flüssigkeitskuppe bis zu deren Gipfelpunkt anzusetzen. Als Prüfungsobjekt kommt zur Zeit wohl nur Quecksilber in Frage. Die an diesem vorgenommenen Messungen weisen bekanntlich grosse Verschiedenheiten auf, weil die Oberflächenspannung gegen Verunreinigungen und gegen die Zusammensetzung der umgebenden Gasatmosphäre sehr empfindlich ist (vgl. die Übersicht bei Bakker (5)). Die Extremwerte für a^2 sind 8,2 (Quincke 1858 und später) und 6,5 (Kernaghan 1931). Wir beschränken uns hier auf Winklers Messungen an »feuchtem» Quecksilber (1). Die Radien

sind dieselben wie bei der Wasserserie, und die vom Autor interpolierten Meniskusvolumina ergeben die in Tabelle 4 zusammengestellten Höhen μ, aus denen man nach Gl. (3) die Kapillarkonstante a^2 berechnet. Der schwache Gang dieser Werte kann auf Versuchsfehlern beruhen; die verlässlichsten Zahlen liegen in der Mitte der Serie.

Tabelle 4.

R	μ	a^2	R	μ	a^2
2	0,52	(8,7)	7	0,73	7,3
3	0,65	7,5	8	0,71	7,6
4	0,71	6,8	9	0,68	7,8
5	0,74	7,2	10	0,65	8,2
6	0,75	7,2	11	0,61	8,3
			12	0,56	8,5

Die hier aufgestellte Formel schliesst sich also in allen betrachteten Fällen mittelgrosser Radien den Versuchsergebnissen mit guter Näherung an. Sie dürfte sich deshalb auch in anderen Fällen zur Berechnung von mittlerer Höhe und Volumen des Meniskus aus Radius und Kapillarkonstante eignen. Da sie gerade in der Nähe des Maximums gut zutrifft, so lässt sich auf sie eine einfache Methode zur Bestimmung der Oberflächenspannung aus Rohrradius und Meniskusvolumen begründen.

Andrerseits scheint aus der Abweichung des von Richards und Carver gefundenen Punktes (Fig. 3) hervorzugehen, dass sie bei sehr grossen Radien zu kleine Werte von μ ergeben kann. In diesem Gebiete stimmt sie auch nicht mit dem von Verschaffelt (2) für sehr grosse Radien abgeleitenen Näherungsausdrucke überein, der seinerseits wieder nicht für mittelgrosse zutreffen kann. Verschaffelt fand als Endresultat

$$h \cdot \sqrt{k} = 0.924 \cdot \sqrt{2\,\pi\, r \sqrt{k} \cdot e^{-r \cdot \sqrt{k}}} \qquad \text{(9)}$$

worin r unserem R entspricht, k gleich $2/a^2$ ist und h die Höhe der Flüssigkeitssäule über dem Nullniveau bis zum tiefsten

Punkte des Meniskus bedeutet. Vereinfacht kann die Formel geschrieben werden

$$h^2 = 3{,}79 \cdot a \cdot R \cdot e^{-2{,}88\frac{R}{a}}$$

und da $h = \frac{a^2}{R} - \mu$, so lässt sich μ berechnen.

Diese Werte für Wasser sind in Fig. 3 durch die gestrichelte Linie dargestellt. Der Punkt von Richards und Carver fügt sich ihr gut ein, für kleinere Radien jedoch weicht sie mehr und mehr nach oben ab. Man kann demnach sagen, dass Verschaffelts Formel etwa an der Stelle zu gelten beginnt, wo unsere Formel (3) zu versagen anfängt. Die Grenze zwischen beiden Ausdrücken liegt etwa bei einem Radius $R = 4.\ a$.

In gewissen praktischen Fällen grosser Radien kann Verschaffelts Formel durch ihre erste Näherung ersetzt werden, d. h. durch die Annahme, dass die Mittelpartie des Meniskus eine nur sehr wenig oberhalb des Nullniveaus liegende Ebene ist ($h \approx 0$) und das Volumen des Meniskus praktisch vollständig in einer schmalen Randpartie enthalten und dem gesamten gehobenen Volumen V gleich ist. Diese Annahme führt übrigens zu der Konsequenz, dass der Vertikalschnitt des Meniskus in der Randpartie einem gleichschenklig-rechtwinkligen Dreieck von der Kathetenlänge a flächengleich ist.

Die untere Grenze, von der an der Meniskus als Halbkugel behandelt werden darf, liegt etwa bei einem Radius von höchstens $a/5$, d. h. für Wasser bei etwas unterhalb 1 mm.

Zusammenfassung.

Es wurden bei 25° in sechs kreiscylindrischen Rohren mit Radien zwischen 2,5 und 7,5 mm die Meniscusvolumina für drei benetzende Flüssigkeiten von den Kapillarkonstanten 10,8, 6,9 und 3,5 mm² bestimmt.

An diesen Werten sowie besonders an einer umfangreichen Literaturserie für Wasser wurde eine Formel geprüft und bestätigt, welche ausser dem Radius als bestimmende Grösse lediglich die Kapillarkonstante, jedoch keinen empirischen Koeffizienten enthält.

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Die potentiometrische Fällungstitration von hochmolekularen Fettsäuren mit Silbernitrat.

Von Per Ekwall und Gösta Juup.

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Bis in die letzte Zeit hinein hat es an einer einfachen Methode gefehlt, die hochmolekularen Fettsäuren nebeneinander analytisch zu bestimmen. Auch die direkte Bestimmung einer einzelnen Fettsäure ist recht umständlich. Der grosse Bedarf nach derartigen Methoden veranlasste uns vor einigen Jahren, die Möglichkeit einer potentiometrischen Fällungstitration der Fettsäuren zu untersuchen. Die meisten Schwermetallsalze dieser Säuren sind bekanntlich schwerlöslich. Wenn die Löslichkeit der Salze verschiedener Säuren sich genügend voneinander unterscheidet, wäre es vielleicht möglich, die Säuren in einer Mischung eine nach der anderen durch potentiometrische Fällungstitration zu bestimmen. Wir teilen hier die Resultate der ersten orientierenden Untersuchung mit, bei welcher die Fettsäuren als Silbersalze gefällt wurden.

Es wurden Stearin-, Palmitin-, Myristin-, Laurin- und Ölsäure in Form ihrer Natriumsalze in wässeriger Lösung mit Silbernitrat titriert. Als Titrierbecher wurden 50 bzw. 100 ccm Bechergläser verwendet. Als Elektrode diente ein neuversilberter Reinsilberdraht. Dieses Halbelement war über einen mit 1-m Kaliumnitratlösung gefüllten elektrolytischen Heber mit einer 1-m Kalomelelektrode (ε cal $= +0{,}283$ V) verbunden. Die elektromotorische Kraft dieser Kette wurde mit einem Siemens Potentiometer gemessen, an dem 0,2 mV noch gut abgeschätzt werden konnten.

Als Titrierflüssigkeit wurden 0,02—0,1-n $AgNO_3$-Lösungen verwendet, welche aus einer 2 bzw. 10 ccm Bürette unter stetiger Umrührung zugeführt wurde. Wegen der Schwerlös-

lichkeit der Alkalisalze der hochmolekularen Fettsäuren war es vorteilhaft oder sogar notwendig, bei höherer Temperatur zu titrieren. Um die Hydrolyse zu unterdrücken, wurde oft etwas Natronlauge zugesetzt.

In Fig. 1 geben wir einige typische Titrationskurven wieder, je eine von der Titration von Laurat, Myristat, Palmitat bzw. Stearat bei 67—70° C. Die Kurven zeigen, dass die Silbersalze sämtlicher erwähnten gesättigten Fettsäuren bei dieser Temperatur noch so schwerlöslich sind, dass ihre quantitative

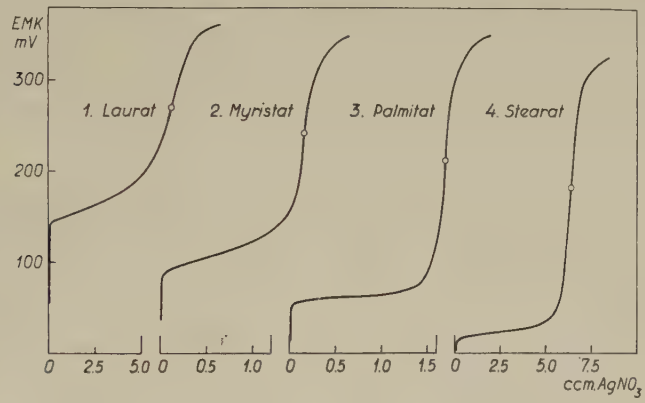

Fig. 1. 1. Titration von 0,00839-n Natriumlaurat mit 0,025-n $AgNO_3$. 67° Fehler —2.4 %.
2. Titration von 0,00814-n Natriummyristat mit 0,05-n $AgNO_3$. 68° Fehler —2,5 %.
3. Titration von 0.01752-n Natriumpalmitat mit 0,1-n $AgNO_3$. 67° Fehler —1.9 %.
4. Titration von 0,00400-n Natriumstearat mit 0,05-n $AgNO_3$. 70° Fehler —3,5 %.

Bestimmung durch Fällungstitration mit Silbernitrat prinzipiell möglich ist. Die Potentialsprünge sind von der Grössenordnung 100—250 mV.

Es wurden Seifenlösungen verschiedener Konzentration titriert. Die Resultate fielen immer etwas zu niedrig aus. So wurden bei sieben Laurattitrationen 1—3 %, bei sieben Myristattitrationen, ebenso 1—3 %, bei sechs Palmitattitrationen 2—3 % und bei dreizehn Stearattitrationen 2—5 % zu niedrige Werte erhalten. Wahrscheinlich wurde immer etwas unverbrauchte Seife von dem Silbersalzniederschlag eingeschlossen. In den beiden letzten Fällen neigte der Fehler dazu grösser

zu werden, wenn die Hydrolyse durch Zusatz von Lauge nicht vorher unterdrückt worden war. Die Hydrolysenprodukte setzen sich voraussichtlich mit dem Silbernitrat sehr langsam um und werden von der Fällung mitgerissen.

Während das Stearat und das Palmitat wegen ihrer Schwerlöslichkeit bei höherer Temperatur, 70—60°, titriert werden müssen, kann das Myristat und vor allem das Laurat auch bei niedrigerer Temperatur bestimmt werden. Bei der Bestimmung der letztgenannten Substanz ist dies sogar vorteilhafter, da die Löslichkeit des Silberlaurats, welche, wie aus Fig. 1 hervorgeht, bei 67° schon recht erheblich ist, mit der Temperatur schnell abnimmt. Die Titration des Myristats kann bei 35° und die des Laurats noch bei 20° gut durchgeführt werden.

Die graphische Darstellung in Fig. 1 zeigt nun weiter, dass die Löslichkeiten der Silbersalze der verschiedenen gesättigten Fettsäuren bei 67—70° sich deutlich von einander unterscheiden. Das Silberlaurat ist am löslichsten, und mit steigender Molekelgrösse der Fettsäure nimmt die Löslichkeit dann recht regelmässig ab. Aus den mitgeteilten Titrierkurven haben wir folgende Löslichkeitsprodukte der Silberseifen bei 70° C berechnet:

Silberlaurat:

Aus dem horizontalen Teil der Kurve,

$$L_{Ag\,L} = 2{,}0 \cdot 10^{-8}.$$

Aus dem Wendepunkt der Kurve (EMK = 270 mV),

$$L_{Ag\,L} = 2{,}7 \cdot 10^{-8}.$$

Silbermyristat:

Aus dem horizontalen Teil der Kurve,

$$L_{Ag\,My} = 3{,}3—2{,}9 \cdot 10^{-9}.$$

Aus dem Wendepunkt der Kurve (EMK = 242 mV),

$$L_{Ag\,My} = 4{,}0 \cdot 10^{-9}.$$

Silberpalmitat:

Aus dem horizontalen Teil der Kurve,

$$L_{Ag\,Pl} = 4{,}3—6{,}8 \cdot 10^{-10}.$$

Aus dem Wendepunkt der Kurve (EMK = 212 mV),

$$L_{Ag\,Pl} = 5{,}3 \cdot 10^{-10}.$$

Silberstearat:

Aus dem horizontalen Teil der Kurve,

$$L_{Ag\,St} = 4{,}0—5{,}7 \cdot 10^{-11}.$$

Aus dem Wendepunkt der Kurve (EMK = 182 mV),

$$L_{Ag\,St} = 6{,}9 \cdot 10^{-11}.$$

Die Berechnungen sind in gewöhnlicher Weise durchgeführt worden. Bei der Berechnung aus dem horizontalen Teil der Titrationskurve muss jedoch beobachtet werden, dass die Aktivität der Fettsäureionen weit unterhalb ihrer Gesamtkonzentration liegen kann. Wie Ekwall und Harva an Lauratlösungen bei 20° gezeigt haben (1), steigt nämlich die Aktivität der Fettsäureionen oberhalb der kritischen Konzentration nicht mehr an, sondern nimmt sogar etwas ab. Bei der Titration von Seifenlösungen, deren Seifengehalt oberhalb der kritischen Konzentration liegt, hat man deshalb im Anfang des horizontalen Teils der Kurve höhere Potentialwerte und einen horizontaleren Verlauf als sonst zu erwarten. Dies ist z. B. bei der Titration der 0,017-n Palmitatlösung und in kleinerem Umfang bei der Titration der 0,004-n Stearatlösung in Fig. 1 der Fall gewesen. Bei der Berechnung der Löslichkeitsprodukte haben wir hier zwischen 0,2 und 1,35 ccm $AgNO_3$ mit dem konstanten Aktivitätswert $a_{Pl'} = 0{,}0032$ bzw. zwischen 1 und 4 ccm $AgNO_3$ mit dem Wert $a_{St'} = 0{,}0012$ gerechnet.

Die nach beiden Methoden berechneten Löslichkeitsprodukte stimmen miteinander gut überein. Als beste Werte für die Löslichkeitsprodukte der Silberseifen bei 70° C können wir also vorläufig angeben:

$$L_{Ag\,L} = 3 \cdot 10^{-8}; \quad L_{Ag\,My} = 4 \cdot 10^{-9}; \quad L_{Ag\,Pl} = 5 \cdot 10^{-10};$$
$$L_{Ag\,St} = 6 \cdot 10^{-11}.$$

Die Löslichkeit der Silberseifen nimmt, wie schon oben hervorgehoben wurde, mit der Temperatur schnell ab. Im Mittel haben wir bei der Titration von Lauratlösungen bei 20—22° den Wendepunkt bei EMK = 269 mV gefunden, woraus man das Löslichkeitsprodukt $L_{Ag\,L} = 3 \cdot 10^{-10}$ bei 20° erhält. Dieser Wert stimmt mit dem von Ekwall und Harva (1) durch Potentialmessungen bei 20° mit einer Silber/Silberlauratelektrode

ermittelten Wert $L_{Ag\,L} = 3—7 \cdot 10^{-10}$ gut überein. Das Löslichkeitsprodukt des Silberlaurats nimmt also von 70° bis 20° um etwa zwei Zehnerpotenzen ab.

Auch die Oleatlösungen können mit Silbernitrat titriert werden und zwar sowohl bei Zimmer- wie bei höherer Temperatur. Lauge muss immer zugefügt werden, weil die verhältnismässig hohe Hydrolyse sonst zu niedrige Werte verursacht. Auch als die Hydrolyse unterdrückt wurde, fanden wir jedoch immer zu wenig Oleat, und zwar bei fünf Titrationen 0,3—3 % zu niedrige Werte. In Fig. 2 führen wir eine Titrationskurve an. Aus derselben errechnen sich folgende Werte für das Löslichkeitsprodukt des Silberoleats bei 70°.

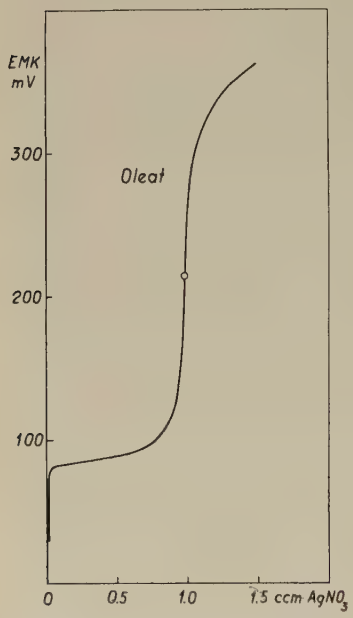

Fig. 2. Titration von 0,00252-n Natriumoleat mit 0,05-n $AgNO_3$. 68°. Fehler −2,7 %.

Silberoleat:

Aus dem horizontalen Teil der Kurve,

$$L_{Ag\,Ol} = 3—8 \cdot 10^{-10}.$$

Aus dem Wendepunkt der Titration (EMK = 214 mV),

$$L_{Ag\,Ol} = 6{,}0 \cdot 10^{-10}.$$

Wir können also vorläufig für das Löslichkeitsprodukt des Silberoleats bei 70° C den Wert $L_{Ag\,Ol} = 6 \cdot 10^{-10}$ angeben. Die Löslichkeit des Silberoleats liegt also zwischen derjenigen des Silberpalmitats und -myristats.

Bei der Titration bei Zimmertemperatur wurde der Wendepunkt bei etwa EMK = 230 mV gefunden. Dies würde bei 20° C das Löslichkeitsprodukt $L_{Ag\,Ol} = 6 \cdot 10^{-11}$ geben.

Die Löslichkeitsprodukte der Silbersalze zweier nacheinander folgender gesättigter Fettsäuren mit gerader Zahl von Kohlenstoffatomen verhalten sich also bei 70°, wie die obigen Zahlen zeigen, etwa wie 8 : 1. Theoretisch lässt sich nachweisen, dass es möglich sein wird, zwei Fettsäuren in einer Mischung nacheinander mit Silbernitrat zu titrieren, wenn ihrer Molekeln

sich durch mehr als zwei CH_2-Gruppen von einander unterscheiden und wenn Mischkristallbildung oder eine starke Adsorption die Titration nicht stört. Dagegen wird es schwierig sein zwei, näher liegende Fettsäuren nebeneinander in dieser Weise quantitativ zu bestimmen. Um dies zu beleuchten, führen wir die theoretisch berechneten Titrationskurven in Fig. 3 an.

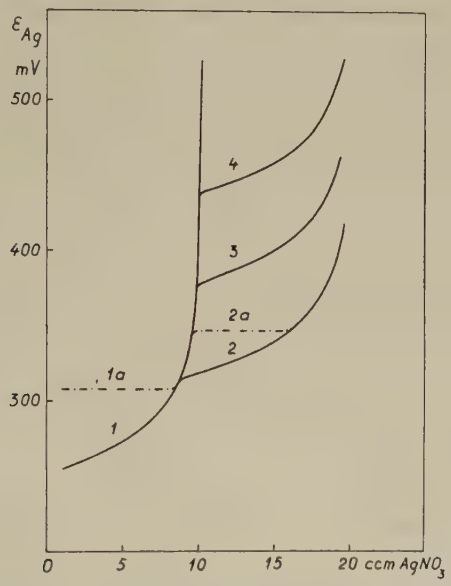

Fig. 3. Theoretisch berechnete Titrationskurven für die Titration von Stearat in Gegenwart einer zweiten gesättigten Fettsäure. 70°.

1—2 Stearat und Palmitat
1—3 Stearat und Myristat
1—4 Stearat und Laurat
} Die Anionenassoziation wird nicht berücksichtigt.

1 a—2 a Stearat und Palmitat. Die Anionenassoziation wird berücksichtigt.

Die Berechnung ist unter der Voraussetzung durchgeführt worden, dass 100 ccm einer Lösung, welche 0,01-n an jeder der anwesenden Seifen ist, mit 0,1-n $AgNO_3$ titriert wird, und dass Silbersalze gebildet werden, deren Löslichkeitsprodukte mit denjenigen des Silberstearats (Kurve 1), -palmitats (Kurve 2), -myristats (Kurve 3) bzw. -laurats (Kurve 4) bei 70° übereinstimmen. Anstatt mit den Aktivitäten der Fettsäureionen, wurde mit ihren Konzentrationen gerechnet.

Die voll ausgezogenen Kurven gelten für den Fall, dass die

Seifen sich wie gewöhnliche Elektrolyte verhalten würden. Sie zeigen, dass bei der Titration von Stearat in Gegenwart von Laurat ein Sprung von etwa 140 mV, bzw. in Gegenwart von Myristat ein Sprung von 70 mV zu erwarten wäre. Ferner geht die Schwierigkeit, Stearat neben Palmitat zu titrieren, deutlich aus den Kurven hervor (Kurve 1—2). Im letzten Falle gehen die Kurvenabschnitte 1 und 2 ohne einen ausgeprägten Sprung in einander über.

Wenn man aber berücksichtigt, dass die Seifen, besonders oberhalb der kritischen Konzentration sich nicht wie normale Elektrolyte verhalten, wird man finden, dass die Möglichkeit zur Titration z. B. des letztgenannten Säurepaars tatsächlich grösser ist, als dies beim ersten Blick erscheint. Wie wir oben hervorhoben, steigt die Aktivität der Fettsäureionen oberhalb der kritischen Konzentration nicht mehr an. Ihr Wert bleibt hier weit unter der Totalkonzentration der Fettsäureionen. Dies wird zu einem viel horizontaleren Verlauf der Titrierkurve beiderseits des Sprunges führen sowie dazu, dass diese Abschnitte bei höheren Potentialwerten verlaufen. Die gestrichelte Kurve 1 a—2 a soll einen derartigen Fall veranschaulichen. Sie ist unter der Voraussetzung berechnet, dass die Aktivität der Stearationen oberhalb der kritischen Konzentration den konstanten Wert 0,0015 und die der Palmitationen den Wert 0,0035 haben. Unter diesen Umständen hat man eine Titrierkurve mit einem ausgeprägten Sprung von etwa 30 mV zu erwarten, und dies öffnet voraussichtlich die Möglichkeit, die beiden erwähnten Säuren, sowie andere ähnliche Säurepaare, zu titrieren.

Wir führten nur vereinzelte Titrationen von Mischungen von zwei Fettsäuren aus. In Fig. 4 werden einige derartige Versuche wiedergegeben. Diese zeigen, dass es tatsächlich möglich ist, Stearat und Laurat, bzw. Stearat und Myristat neben einander zu bestimmen. Theoretisch kann vorausgesehen werden, dass die Stearatbestimmung in diesen Fällen zu niedrige Werte geben muss, weil Silberlaurat und vor allem Silbermyristat auszufallen beginnt, bevor alles Stearat gefällt worden ist. Für die Menge der löslicheren Seife hat man deshalb zu hohe Werte zu erwarten. Im ersten Fall wurden 2 % zu wenig

Stearat und 2 % zu viel Laurat, in zweitem Fall 3,8 % zu wenig Stearat und 1 % zu viel Myristat gefunden.

Auch in Gegenwart von Oleat scheint Stearat bestimmt werden zu können, wie aus der dritten Kurve in Fig. 4 hervorgeht. Die Endpunktsbestimmung bei der Stearattitration war jedoch hier recht ungenau. Es wurden etwa 8 % zu wenig Stearat und etwa 3 % zu viel Oleat gefunden.

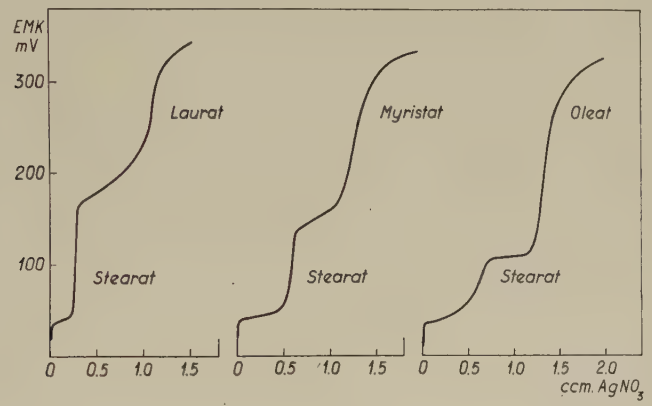

Fig. 4. 1 Titration von 0,00189-n Natriumstearat und 0,00405-n Natriumlaurat mit 0,1-n $AgNO_3$. 67°.

2 Titration von 0,00164-n Natriumstearat und 0,00171-n Natriummyristat mit 0,05-n $AgNO_3$. 69°.

3 Titration von 0,00163-n Natriumstearat und 0,00190-n Natriumoleat mit 0,05-n $AgNo_3$. 69°.

Es wurden dann noch einige Titrationen von Mischungen mit 3—5 verschiedenen Fettsäuren ausgeführt. In diesem Zusammenhang mag nur erwähnt werden, dass es im allgemeinen möglich zu sein scheint, die Gesamtfettsäuremenge innerhalb —3 % zu bestimmen.

Die Untersuchung ist später am Physikalisch-chemischen Institut der Universität, Uppsala fortgesetzt worden.

Zusammenfassung.

Es wird gezeigt, dass eine potentiometrische Fällungstitration der hochmolekularen Fettsäuren mit Silbernitrat möglich ist.

Einzelne Fettsäuren können mit einem Titrationsfehler von

höchstens —5 % bestimmt werden. Dasselbe gilt für die Bestimmung der Gesamtmenge einer Fettsäuremischung.

Die Löslichkeiten der Silbersalze verschiedener Fettsäuren unterscheiden sich deutlich voneinander. Die Löslichkeitsprodukte der Silbersalze werden aus den Titrationskurven approximativ bestimmt und anhand dieser Werte wird die Möglichkeit zur Bestimmung von zwei verschiedenen Fettsäuren nebeneinander diskutiert. Theoretisch und experimentell wird gezeigt, dass eine derartige Bestimmung möglich ist, wenn die Kohlenwasserstoffketten der Fettsäuren sich durch mehr als zwei CH_2-Gruppen von einander unterscheiden. Bei der Titration von zwei naheliegenden gesättigten Fettsäuren mit gerader Zahl von Kohlenstoffatomen können Schwierigkeiten vorausgesehen werden. Eine potentiometrische Bestimmung beider Säuren scheint doch auch in diesem Falle aussichtsreich.

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Eingegangen am 19. Mai 1944.

Framställning av kalisalter ur svensk råvara.

Av J. Arvid Hedvall och Sven Nordengren.

I tider av krig och avspärrning är det av största vikt att jordbrukets produktion kan upprätthållas. Det kan emellertid endast ske om tillgången på konstgödselmedel är tillräcklig. Man behöver därvid inte ha så stora kvantiteter till förfogande som användas i fredstid, enär ett visst slöseri nog förekommer på en del jordar, men en väsentlig del av fredsförbrukningen bör kunna tillhandahållas. Det gäller därvid att ha tillgång till såväl fosforsyra som kväve och kali, enär ett överskott av ett växtnäringsmedel inte kan ersätta underskott av ett annat.

Under nu pågående krig har det lyckats oss att lösa den viktiga frågan om jordbrukets försörjning med fosfatgödselmedel ur svensk råvara. Den nuvarande produktionen av apatitkoncentrat vid de norrländska malmfälten ger oss möjlighet att producera lika mycket superfosfat som förbrukades i Sverige åren före kriget. Halten är emellertid lägre, 13—14 % i stället för 20 %, men den mängd fosforsyra, omkring 70 % av toppförbrukningen före kriget, som på detta sätt kommer det svenska jordbruket till godo, är om än knapp dock tillräcklig för att säkerställa en god skörd.

Av kvävehaltiga gödselmedel producera vi själva en del, och importen har kunnat försiggå i önskvärd omfattning. Emellertid utbyggas för närvarande de svenska kvävefabrikerna så att vi inom kort inom landet få en produktion även av kvävegödselmedel motsvarande 70 % av förkrigsförbrukningen. Denna produktion täcker likaledes det väsentliga behovet.

Av kali ha vi kunnat importera vad vi behöva, men skulle denna import av något skäl upphöra, skulle vårt lantbruk stå helt utan detta viktiga växtnäringsmedel.

Det är därför av synnerlig vikt att söka åstadkomma en produktion av kali inom landet. Även om den inte omedelbart kunde täcka så stor del av förbrukningen skulle den vid avspärrning kunna utbyggas. Det gamla problemet att ur svensk råvara framställa kalisalter främst för gödningsändamål har därför ånyo tagits upp.

I korthet må av tidigare arbeten i denna riktning följande omnämnas.

Igelström föreslog 1868 att smälta kalifältspat och kalk så att en slagg löslig i syra erhålles. Åtgången av syra blir dock ganska betydande och metoden dyr.

I början av 1900-talet föreslog Dahlerus att beskicka en masugn med alunskiffer eller skifferaska, kalksten och något kol, varjämte något järnmalm skulle tillsättas. Vid reduktionen av järnmalmen skulle alkalierna förflyktigas och uppsamlas i säckfilter. Järnet i skiffern samt i järnmalmen skulle ge tackjärn. Försök härmed ha utförts vid Degerhamn på Öland.

Enligt Lindblads och Yngströms elektrokalimetod (1912) blandas fältspathaltigt material i en elektrisk smältugn med kol och järnskrot, varvid vid 1 800° kolet delvis reducerar fältspatens kiselsyra till kisel, som förenar sig med järnet till kiseljärn. Härigenom minskas kiselsyremängden i kaliumaluminiumsilikatet, som på så sätt blir lösligt i syror.

Enligt Radmanns kalikalkmetod (1917) blandas 1 del fältspat, 1 del kalksten och $^1/_2$ del gips och briketteras samt bränes i en vanlig tegelringugn vid 1 150°. Kalit övergår härvid till sulfat. Av leptit med 10 % kali erhölls en produkt med c:a 5 % kali, som antingen kan lakas eller användas direkt. Metoden kan tyvärr ej utföras, då gips ej finnes inom landet i erforderliga kvantiteter.

En kalimetod, som ledde till utförande i stor skala och som utprovades under flera års drift, är Jungners kalicementmetod. Ur röken från cementugnarna utskildes kali i elektriska stoftkamrar. En dylik fabrik kom till stånd vid Slite på Gotland, men den nedlades efter hand och maskinerna togos bort.

Hultman, Collenberg och Gustafsson ha arbetat med problemet att utvinna kali ur den vid oljeutvinning ur skiffer bildade skifferkoksen. Denna smältes i elektrisk ugn, eventuellt med tillsats även av kalk, vid sådan temperatur att större delen

av järnet utsmältes i form av kiseljärn, varvid den erhållna slaggen granuleras i vatten. Granulatet urlakas med svavelsyra. Ur den så erhållna lösningen utfälles kalialun med hjälp av kaliumsulfat, som går i cirkulation. Ur kalialunlösningen, som är praktiskt taget fri från kiselsyra, järn m. m., utfälles aluminiumhydrat medelst kaliumsulfhydrat, som ävenledes går i cirkulation. Aluminiumhydratet överföres till aluminiumoxid, och det kali, som icke cirkulerar i processen, utvinnes som kaliumsulfat. Enligt en modifikation av detta förfarande sker utlakningen med hjälp av svavelsyrlighet. Försök i halvstor skala pågå med denna metod.

För att vara lönande fordrar sistnämnda metod att aluminiumoxid eller annan aluminiumförening tillgodogöres. Detta gör givetvis metoden mera komplicerad och mindre ägnad att i stor skala kunna improviseras, om så kräves. Vi ha därför sökt andra utvägar varigenom kalisalter skulle kunna tillverkas ur svensk råvara.

Vår första undersökning gällde, huruvida man vid behov skulle kunna få fram erforderliga kvantiteter kali ur cementfabrikernas rökgaser. Denna undersökning har givit ett negativt resultat. De flesta cementfabriker i Sverige införa numera råmassan i ugnarna i uppslammad form. Om kalihalten i råvaran ökas, kommer större delen att stanna i cementklinkern, som härigenom blir av sämre kvalitet. Att omändra cementtillverkningen så att en återgång sker till det tidigare använda torrförfarandet kan ej komma i fråga. Även om så kunde ske skulle man med de råvaror som stå till buds ej kunna utdriva mer än 25—30 kg rent kali per ton cementklinker. Beräknas den nuvarande tillverkningen av cementklinker till c:a 500 000 ton per år, skulle detta motsvara en kaliutvinning av omkring 12 000—15 000 ton K_2O. Minimibehovet inom landet kan emellertid uppskattas till åtminstone 20 000 ton K_2O per år. Den nuvarande förbrukningen är omkring 36 000 ton,

Det blev sålunda nödvändigt att undersöka, huruvida medelst ett direkt uppslutningsförfarande någon svensk råvara skulle kunna bearbetas. Den kalihaltiga återstoden av alunskiffern efter oljans avdrivning är otvivelaktigt vårt billigaste kalihaltiga råmaterial, då det utfaller som avfall. Man kan er-

hålla ungefär lika mycket rent kali (K_2O) ur skiffern som olja, och kali är en mycket värdefullare produkt än olja. Den mängd kali, som finnes i den skifferaska och skifferkoks som årligen utfaller vid oljeverken i Kvarntorp och Kinne-Kleva, överstiger Sveriges nuvarande kaliförbrukning för gödslingsändamål. — Dessutom kunde man tänka sig att utgå från fältspat, glimmer, leptit eller andra kalihaltiga mineral som finnas i landet.

Undersökningens planläggning.

Alltsedan Justus von Liebigs banbrytande arbeten om markkemi och växternas näringsfysiologi i mitten av förra århundradet har i hastigt ökad takt en litteratur på det nya agrikulturkemiska området växt fram. De tidigaste analytiska arbetena utökas mycket snart med undersökningar av möjligheten att framställa konstgödsel, alltså syntetiska kali-, fosfor- eller kvävepreparat. Det dröjer ej heller länge innan de uttagna patenten bli legio.

Vad kalit beträffar, så gå samtliga föreslagna metoder ut på, att ur kalihaltiga mineral eller bergarter — exempelvis fältspat, glimmer, leucit, leptit, gnejs — framställa kalit i löslig form. Man finner självfallet, att patenten äro talrikast i sådana länder, som sakna naturliga kaliförekomster. Men även Tyskland har, trots sina saltlager, ett mycket stort antal uppfinningar på detta område både i äldre och nyare tid.

Som redan inledningsvis antytts så har man vid arbeten av denna art slagit in på olika principvägar, allteftersom det gällt att framställa kalipreparaten med eller utan värdefulla biprodukter. Det har också visats att Sverige i intet avseende utgör något undantag från det nu anförda förhållandet.

Då vårt arbete påbörjades uppdrogo vi vissa önskvärda riktlinjer i fråga om metodiken. Detta skedde med tanke på att kunna använda inom landet redan förefintlig industriell utrustning, dels för provkörning i teknisk skala, dels ock för en hastigt startad fabrikation för det fall att någon lämplig metod kunde framkomma och förhållandena så fordrade. Det var närmast utsikten att få disponera över någon eller några

av cementindustrins roterugnar, som dikterade det uppställda villkoret, att vid så låg temperatur att smältning och därigenom vållad förstörelse av ugnsväggarna ej inträdde upphetta lämpliga blandningar av den kalihaltiga råvaran. Om det visade sig möjligt att under dessa förutsättningar genomföra en dekomposition med gott utbyte, så skulle dessutom den fördelen vinnas, att den frigjorda kaliföreningens förflyktigande i görligaste mån hindrades.

Under dessa förutsättningar kunde redan från början experimenten inriktas på framställning av kali i någon av formerna klorid, sulfat, hydroxid eller karbonat.

Vid användning av ugnar av nyssnämnd typ men med undvikande av höga temperaturer och kalits förflyktigande kunde av dessa föreningar knappast andra än kloriden och sulfatet ifrågakomma. Hydroxiden och eventuellt även karbonatet förutsätter förflyktigande, såvida man ej, vad det senare beträffar, ville uppsluta med soda, vilket emellertid av ekonomiska skäl var uteslutet. Tog man sikte på produktion av hydroxid eller karbonat med enklast möjliga apparatur, var det från början klart, att man borde gå en helt annan väg och i stället föredraga en autoklavbehandling.

I fortsättningen skall lämnas en översikt över utförda experiment enligt de olika förfaringssätten, vilka lett till *tre olika metoder, som var för sig innebära möjligheten av inhemsk framställning av kali.* Två av dem torde väl i varje fall ej utan sammankoppling med biproduktsframställning kunna komma till användning annat än under av krig framkallade avspärrningsförhållanden; den tredje, som nu skall utprovas i halvstor skal, synes däremot ha utsikter att kunna bestå även i fredstid och göra vårt land mindre beroende av import av en av vår hushållnings viktigaste produkter.

En genomgång av den in- och utländska patentlitteraturen visade som väntat, att alla ekonomiskt tänkbara (och ej sällan även andra!) uppslutningsmetoder försökts. För högtemperaturbehandling kunna ju knappast andra inblandningar än kalk, klorkalcium, gips och koksalt komma ifråga, och vid autoklavmetodik måste det verksamma medlet vara tryckånga, eventuellt under samtidig inverkan av någon eller några av nämnda substanser.

Det var således som nämnt klart att experimentarbetet ej borde inriktas på sökandet efter *i princip* nya metoder. Med vår nuvarande kännedom om fasta substansers av struktur eller föroreningar mer eller mindre starkt beroende men alltid förefintliga individualitet i avseende på reaktionsförmåga, så stod det emellertid lika klart, att säkerligen intet i litteraturen beskrivet förfaringssätt skulle visa sig direkt användbart under de förutsättningar, som tekniskt ekonomiska och med hänsyn till råmaterialet även lokala faktorer nödvändiggjorde. Orienterande stickprov enligt metoder som kunde vara av intresse bekräftade undantagslöst denna förmodan. Visserligen erhöllos reaktionsprodukter av uppgiven typ, men utbytet stämde ej med angivna värden. Vad beträffar uppslutningsmetoderna genom tillsatser och upphettning till höga temperaturer, så var för övrigt ej mycket att hämta ur litteraturen, då man i regel arbetat vid avsevärt högre värmegrader än vad som för dessa arbeten ansågs önskvärt.

De orienterande försöken fastslogo således nödvändigheten av att till ett visst råmaterial synnerligen noga anpassa reaktionsbetingelserna, d. v. s. att åstadkomma den bästa möjliga kombinationen av följande variabla faktorer: arten av tillsatsmedel, blandningens proportioner och kornstorlek, tid och temperatur för upphettningen samt den omgivande gasens egenskaper.

Under det att i dessa avseenden en nästan avskräckande mångfald av kombinationsmöjligheter synes erbjuda sig, så var av skäl, som i denna uppsats redan inledningsvis anförts, valet av kalihaltigt råmaterial i det närmaste på förhand givet, då det av olika anledningar visat sig i hög grad önskvärt att på något sätt nyttiggöra avfallet från skifferdestillationsverken. Dessa fördelar ansågos så stora, trots askans relativt låga halt av K_2O (maximalt c:a 5 %), att andra kalirikare råmaterial, t. ex. leptit, icke i första hand borde ifrågakomma. Vid försöken har då intet annat nämnts en aska från Bergh-ugnarna i Kvarntorp, hållande c:a 4,9 % K_2O använts.

Vid samtliga metoder nedmaldes askan och de använda tillsatserna så att de passerade en sikt av 1 600 maskor/cm^2. Vid de experiment, där höga temperaturer förekommit, ha omsorgsfullt blandade massor i önskade proportioner upphettats i

oglaserade porslinsskepp, vilka insatts i elektriskt värmda ugnar med tillräckligt stort område för temperaturkonstans. Temperaturen har mätts med termoelement med en noggrannhet av $\pm$ 3°. Medelst olika behållare och gashastighetsmätare kunde gasens sammansättning och överledningshastighet noga kontrolleras. För att erhålla entydiga resultat varierades givetvis endast en faktor åt gången i en jämförelseserie.

Efter reaktionstiden uttogos skeppen (dubbelprov), och den endast löst sammanbakade och vid skeppen ej häftande produkten nedfördes snabbt i destillerat vatten. Den lätt desintegrerade massan kokades med vatten i 30 minuter samt späddes till lämplig volym, varefter centrifugerades och analyserades i avseende på kalihalt enligt Kramer-Tisdalls metod (Fresenius-Jander, Handb. d. analyt. Chemie *1940* I:a, sid. 186—191). Resultatet anges såsom utbyte av vattenlösligt K_2O, resp. vattenlösligt + avrykt K_2O i % av askans K_2O-halt.

I det följande lämnas en kortfattad redogörelse för de viktigaste uppnådda resultaten. Av det mycket stora antalet utförda försök ha självfallet endast de medtagits, som svara mot betingelserna för goda utbyten eller som, där detta ej är fallet, varit ägnade att klarlägga principiellt viktiga reaktionsfaktorer. Vi ha kallat de tre metoder, som framkommit vid laboratorieundersökningen, för *koksaltmetoden*, *svavelkismetoden* och *autoklavmetoden*. Vid dessa arbeten ha civling. Sandford och dåvarande teknologerna Hällestam och Johansson biträtt.

I. Koksaltmetoden.

Utbytets beroende av blandningens sammansättning samt av reaktionstid och temperatur.

Av provade inblandningar (CaO, $CaCO_3$, $CaCl_2$ och NaCl) visade sig $CaCO_3$ + NaCl förmånligast. Dekompositionen går bra även med CaO eller $Ca[OH]_2$ i stället för $CaCO_3$. Då emellertid inga störningar genom användning av $CaCO_3$ uppträda, så föredrogs denna form av kalk, som ger fördelen att slippa extra bränning. En behandling med kalk och koksalt är även i tidigare använda metoder vanlig. Vilka reaktioner

som inträffa vid upphettning har tidigare ej mycket diskuterats. Med så vagt definierade substanser som skifferaska eller liknande är detta givetvis också skäligen vanskligt att i detalj angiva.

Vid föreliggande arbeten var det emellertid överhuvud taget och framför allt för att nedbringa antalet förförsök nödvändigt att uppställa en hypotes för reaktionsförloppet. Det syntes då rimligt antaga, att kalit i askan förekommer bundet på ett fältspatliknande sätt. Tidigare (t. ex. från den bekanta Jungnermetoden) är känt, att kalit vid mycket hög temperatur låter sig avdestilleras. Nu utförda experiment ha visat, att den kalifrigörande reaktionen i närvaro av CaO börjar redan vid betydligt lägre temperaturer, långt före uppträdandet av någon smälta. Processen kan således uppenbarligen förlöpa som en pulverdekomposition (platsväxlingsreaktion (jfr litt.-förtekn. 1)), där Ca inträder i stället för K. Den likaledes tidigare använda koksalttillsatsen torde kunna ha en tvåfaldig betydelse, i det att en inverkan både som flussmedel och som reaktionsdeltagare är sannolik. Med försökstemperaturen varierar dessa rollers inbördes förhållande. Av våra försök, vilka även för så låga temperaturer att någon smälta ej uppträder visa en utbytesbefordrande inverkan av NaCl, framgår att koksaltet får tillmätas en viktig roll som reaktionspartner (fast, flytande eller gasformigt). Man kan då antaga att kalk och natron tillsammans med kiselsyra och lerjord ge olösliga plagioklasliknande produkter (motsvarande är ej känt för Ca + K). Ett med en större kvantitet aska utfört analysprov för att erhålla ett begrepp om vart de olika tillsatserna taga vägen och hur mycket koksalt som kan återvinnas (jfr nedan sid. 124—125) har givit gott belägg för den uppställda arbetshypotesen.

Försök utfördes nu för att utröna med vilka minsta möjliga mängder av kalk och koksalt ett gott utbyte av utlösbar KCl kunde erhållas. För att slippa komplikationer genom förflyktigande av KCl och NaCl valdes vid dessa försök en temperatur (750°) lägre än den för bästa utbyte sannolika. Följande kurvor (Fig. 1 och 2) angiva de erhållna resultaten. Under de använda betingelserna i övrigt (60 minuter, lufttorr CO_2-atmosfär) finnes således ingen anledning öka inblandningen av $CaCO_3$ till mer än 50 viktsdelar per 100 viktsdelar aska

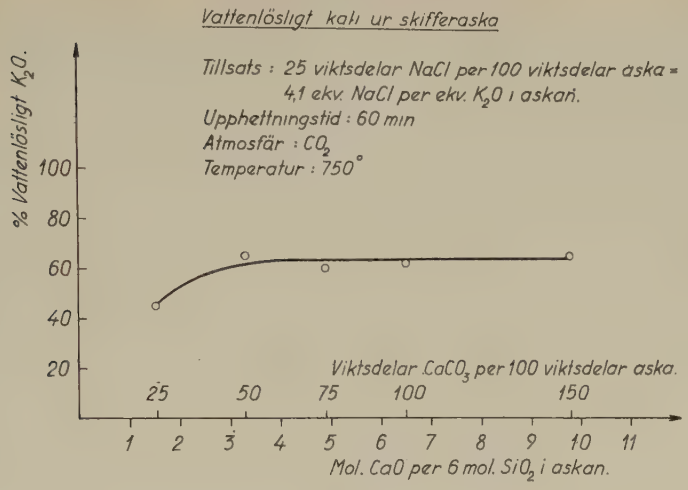

Fig. 1.

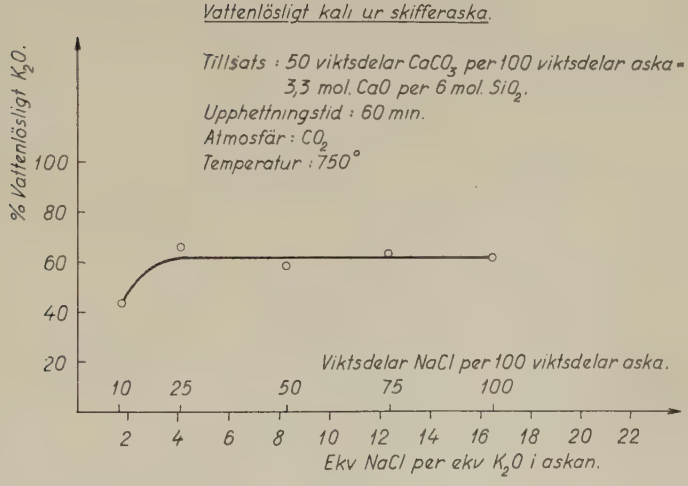

Fig. 2.

(= 3,3 mol CaO per 6 mol SiO_2 i askan). Under denna mängd CaO inträder dock nedsättning i utbytet. Enligt Fig. 2 gäller, att under samma reaktionsbetingelser NaCl-halten bör hålla sig vid c:a 4 mol per mol K_2O i askan (= 25 viktsdelar NaCl per 100 viktsdelar aska). Under dessa betingelser synes ett

maximalt utbyte av c:a 65 % det teoretiska kunna erhållas i form av ur reaktionsprodukten urlakbar KCl. Nämnvärda mängder förflyktigad KCl förekommer ej.

Det nämnda utbytet kan under för övrigt använda försöksbetingelser icke uppnås med kortare upphettningstider än c:a 60 minuter. Med bibehållande av förutvarande relativa mängder $CaCO_3$ och NaCl visade sig utbytet stiga med c:a 10 % vid höjning av temperaturen till mellan 900° och 1 000°, trots att upphettningstiden sänkts till hälften. En ökning av NaCl-mängden förbättrar utbytet ytterligare, och vid 6,6 mol Na_2O per K_2O blir den utlösbara KCl-mängden redan vid omkring 900° c:a 90 % under bibehållen reaktionstid av 30 minuter. En höj-

Tabell 1. Atmosfär: lufttorr CO_2.

Blandning per 100 g aska				Upphettnings-		% vattenlöslig K_2O räknad på teoretiskt totalutbyte	Massans konsistens
Mol CaO per 6 SiO_2 i askan	NaCl i ekv. K_2O i askan	$CaCO_3$	NaCl	-temp. °C	-tid, min.		
3.3	3,3	50	20	840	30	73	osintrad
»	»	»	»	915	»	»	»
»	»	»	»	925	»	»	»
»	»	»	»	1 010	»	70	»
»	5,0	»	30	1 000	»	85	»
»	5,6	»	34	915	»	77	»
»	6,6	»	40	810	»	74	»
»	»	»	»	870	»	85	»
»	»	»	»	915	»	86	»
»	»	»	»	960	»	91	»
»	»	»	»	1 010	»	90	»
»	»	»	»	1.060	»	ej best.	sintrad
4,0	1,4	65	8,5	950	240	0 (allt avrykt)	osintrad

I tabellen har till komplettering av de betingelser och resultat, som svara mot fig. 1 och 2, även medtagits några extremvärden beträffande reaktionspåverkande faktorer. Som synes kan NaCl-tillsatsen minskas avsevärt, om man samtidigt nöjer sig med något nedsatta utbytessiffror. Vid långa reaktionstider ryker allt KCl bort, t. o. m. utan närvaro av NaCl.

ning av temperaturen över 900° medför knappast några fördelar, emedan den växande mängden förflyktigad KCl sänker utbytet av ur reaktionsprodukten utlösbar klorid. Jfr Tab. 1. Tiden 30 minuter är för övrigt i överkant. Den kan utan nämnvärd minskning i utbyte med den använda apparaturen sänkas till hälften. Kombinationen av tid och temperatur för upphettningen blir i stordrift en fråga, som starkt influeras av ugnskonstruktionen. Med tanke på NaCl-återvinningen måste tillsatsen alltid hållas så låg som möjligt.

Ugnsatmosfärens inverkan.

Olika kombinationer av i tekniken förekommande ugnsgaser (CO, CO_2, luft, H_2O) ha provats. Vattenånga eller fuktiga gaser befordra i allmänhet dekompositionen, men denna fördel uppväges eller motverkas därav att kalits förflyktigande likaledes i hög grad befrämjas genom närvaro av H_2O i ångform. De bästa utbytena ha erhållits av torr CO_2-haltig atmosfär, vilket ju också svarar väl till vad som kan förekomma i stordrift. Under dessa förhållanden äro de förut nämnda resultaten erhållna.

Under senare år har en serie undersökningar utförts (2), vilka visat den omgivande gasatmosfärens stora betydelse för reaktionsutbytet vid pulverreaktioner, i det att även i vanlig kemisk mening icke aggressiva gaser kunna inverka. Därigenom att gaserna i högre eller lägre grad lösas upp i de fasta kornen ändras i reagerbara blandningar utbytet, dels direkt genom ändrad ytaktivitet, dels indirekt genom ändrade rekristallisationshastigheter och därav framkallade ändringar i kontaktytans storlek. Ehuru variationer i den omgivande atmosfärens sammansättning även på annat sätt kunna inverka på den hastighet varmed ett flyktigt ämne kan avlägsnas ur massan, så är det tydligt, att även faktorer av det slag, som nu nämnts, böra utöva inflytande. Här har redan anförts, att vattenånga befordrar bortgången av kalit under det att CO_2 verkar i motsatt riktning. Följande försök visa i jämförelse med förut erhållna resultat i CO_2-atmosfär, att luft i mindre grad än CO_2 håller tillbaka mängden »avrykt kali».

Balanskalkyler för processen.

En viktig del av processen består i möjligheten att återvinna koksaltet. Därför och för att i görligaste mån få ett begrepp om reaktionsförloppet ha försök utförts, vilkas resultat framgå av följande tablå:

Charge.

100 Bergbaska
50 $CaCO_3$
40 NaCl

} 20,52 g, innehållande 10,80 g aska, invägdes i alundumdegel, upphettades 60 min. vid 900° liksom förut i rörugn men *i luft.*

Resultat.

Vattenlösligt kali	= 3,37 %	Utbyte 69 %
Kali i återstod	(= 0,57 %)	
Avrykt kali	= 0,92 %	» 19 %
Totalt utvunnet kali	= 4,29 %	Utbyte 88 %

Av ovanstående charge erhölls efter utlakning och indunstning 3,979 g salt, som befanns innehålla

K = 7,6 %	= 0,195	ekvivalenter	
Na = 26,6 %	= 1,154	»	
Ca = 4,6 %	= 0,230	»	summa katjoner = 1,579
Cl = 48,1 %	= 1,355	ekvivalenter	
SO_4 = 11,0 %	= 0,229	»	summa anjoner = 1,584
olösl. = 0,1 %			
98,0 %			

Rationell sammansättning av saltblandningen.

14,5 % KCl
67,6 % NaCl
15,6 % $CaSO_4$

Balans över K, Na och Cl.

Chargen 20,53 g =
- 10,80 g aska med 4,03 % K och 0.24 % Na
- 4,32 g NaCl
- 5,40 g $CaCO_3$

In			Ut		
	g	ekv.		g	ekv.
Na:			Na:		
Med askan	0,026	0,11	Utlöst	1,061	4,61
Tillsatt NaCl	1,700	7,39	Kvar olösl. i rest . .	0,229	0,99
			Avrykt	0,486*	1,00*
	1,726	7,50		1,726	7,50
K:			K:		
Med askan	0,436	1,11	Utlöst	0,302	0,77
			Kvar olösl. i rest . .	0,051	0,13
			Avrykt	0,083*	0,21*
	0,436	1,11		0,436	1,11
Cl:			Cl:		
Tillsatt NaCl	2,62	7,39	Utlöst	1,91	5,39
			Avrykt	1,71*	2,00*
	2,62	7,39		2,62	7,39

De med * betecknade värdena på det avrykta äro beräknade som differenser mellan de övriga analyserna.

Avrykt K + Na = 2,11* ekv. Avrykt Cl = 2,00* ekv.

Viktsbalans:

In			Ut	
	g			g
Charge: Berghaska	10,80	Utlakat salt		3,98
Charge: NaCl	4,32	Olösl. återstod, torkad . . .		12,40
Charge: $CaCO_3$	5,40	8,99 % glödgn. förl. hos askan		0,97
SO_3 ur SO_4 i det urlakade .	0,37	Avrykt NaCl + KCl		1,23
(O_2 ur luft eller CO_2 och S ur glödgn. förl. hos askan)		CO_2 bort ur $CaCO_3$		2,38
	20,89			20,96

Medräknas det avrykta saltet som utbyte fås:

Tillsatt	Utvunnet
4,32 g NaCl	3,81 g NaCl = 73,7 % av 0,74 g KCl = 14,3 % » 0,62 g $CaSO_4$ = 12,0 % » 100,0 — 5,17 g salter

Av ovanstående framgår, att i stället för 0,98 ekv. utvunnet kalium 0,88 ekv. natrium går in i silikatet i olöslig form. Reaktionen är alltså vad beträffar dessa ämnen i huvudsak en utbytesreaktion enligt:

olösligt K-Al-silikat + NaCl → olösligt Ca-Na-Al-silikat + KCl.

Härmed stämmer också resultaten av försök att utföra dekompositionen med KCl istället för med NaCl. Det visar sig nämligen att kaliumkloridens inverkan är högst betydligt mindre än natriumkloridens.

Av ett visst intresse bl. a. för följande metod II är, att det kalcium som utlösts förekommer som sulfat och ej som klorid, så när som på mycket små spår (pyridin utlöste nästan intet) vilket även framgår av att ekvivalenttalen för utlakad Ca^{++} och SO_4^{--} äro lika.

Det utlakade saltet kommer alltså att bestå av alkaliklorider, i mycket ringa grad förorenade av sulfater. Aluminium i löslig form (salt eller oxid) har ej kunnat påvisas (vatten resp. natronlut) som lösningsmedel. Då metoderna att skilja dylika salter åt sedan länge äro bekanta och för övrigt starkt bero av den renhetsgrad man önskar, skall denna fråga här ej behandlas. I huvudsak gäller det givetvis återvinningen av NaCl. Av Tab. 1 framgår att den tillsatta mängden av detta salt kan avsevärt varieras, alltefter det utbyte av KCl man fixerar som tillräckligt.

Kompletterande försök med andra utgångsmaterial.

Metodiken var oförändrat densamma som med askan i det föregående.

Försök med leptit av K_2O-halt = 11,0 %.

Då enligt i inledningen framlagda förhållanden åtminstone för närvarande icke något större intresse föreligger för användning av denna råvara, meddelas här endast ett kort utdrag ur resultaten från företagna experiment. Högre utbyten av KCl erhållas först vid en något större $CaCO_3$-tillsats (4 mol CaO per 6 mol SiO_2 i leptiten eller 72,4 g $CaCO_3$ per 100 g leptit) än vid försöken med askan. Utbytena växa vid ytterligare $CaCO_3$-tillsats men endast med ett par procent vid en ökning av CaO till det dubbla, ett förhållande, som alltså saknar praktiskt intresse.

Vid användning av 72,4 g $CaCO_3$ per 100 g leptit och 1,25 ekv. NaCl per K_2O (17,1 g NaCl per 100 g leptit) uppnåddes under 60 minuters upphettning i lufttorr CO_2 vid 750° (alltså motsvarande askförsöken i Fig. 1 och 2) aldrig mer än 30 % löslig KCl. Avsevärda mängder förflyktigades (10—30 %). I likhet med förfarandet vid experimenten med aska utprovades bästa möjliga utbyte av kvarstannande löslig KCl genom höjning av NaCl-halten och temperaturen och sänkning av reaktionstiden. Ett optimum erhölls därvid under följande kombination av betingelser:

4 CaO per 6 SiO_2 i leptiten, 5 ekv. NaCl per K_2O (72,4 g $CaCO_3$ + 68,5 g NaCl per 100 g leptit) vid 950° under 15 minuter. Därvid erhölls 66,5 % löslig och 15 % förflyktigad KCl. Vid 850° motsvaras siffran 66,5 % av 58,5 % (löslig KCl alltså).

Det förtjänar påpekas, huru olika leptiten uppträder vid jämförelse med askan, ett förhållande, som illustrerar de i inledningen nämnda individuella reaktionsegenskaperna hos olika material och som understryker den även från andra områden väl kända omöjligheten att direkt söka tillämpa patentdata. Fuktig atmosfär påskyndar även för leptiten dekompositionsförloppet men befordrar liksom vid askan förflyktigandet.

Det kan ha sitt värde att omnämna, att försöksserier med konstgjord förvittring av leptiten utförts, i det att den upphettades i $H_2O + CO_2$ vid olika temperaturer före inblandningen av $CaCO_3$ och NaCl. En dylik behandling medförde emellertid ingen som helst förbättring med hänsyn till vattenutlösbar KCl, snarare tvärtom. Däremot steg som väntat lösligheten i H_2SO_4.

Försök med andra slag av skifferaska och med obränd skiffer.

Vid skifferoljeverkens destillation faller även en aska med annan sammansättning än den från Berghugnarna. Industrimetoders ugn ger den s. k. skifferkoksen som, svarande mot benämningen, fortfarande besitter ett visst värmevärde. Försöksserier ha utförts även med detta material, vilket besitter ett stort intresse, eftersom denna koks senare visat sig användbar för kalkbränningen (jfr nedan). Utan anförande av data skall här endast nämnas, att skifferkoksen under likartade betingelser i övrigt förhåller sig fullt analogt med Berghaskan med hänsyn till utbytet av vattenlöslig KCl.

På enahanda sätt förhåller sig också den *odestillerade skiffern*. Det torde således från kaliutvinningssynpunkt sett vara möjligt att med lämplig ugnskonstruktion direkt blanda skiffern med kalk och koksalt och erhålla vattenlöslig KCl i askan, sannolikt dock med större halt av K_2SO_4. Hur en dylik kombination skulle inverka på destillationsförloppet har fallit utom ramen för detta arbete att undersöka.

II. Svavelkismetoden.

Som under metod I omnämnts uppkommer vid upphettningen även något $CaSO_4$ och K_2SO_4. Bildandet av $CaSO_4$ är att tillskriva en typ av pulverreaktioner, som först för ett tjugotal år sedan upptäcktes (3). I föreliggande fall äger omsättningen rum enligt formeln:

$$4\,CaO + 2\,FeS_2 + 7{,}5\,O_2 = 4\,CaSO_4 + Fe_2O_3$$

och startar redan strax ovan 500°. Det bildade kalciumsulfatet skulle normalt sönderfalla under utveckling av SO_3 eller $SO_2 + O_2$ först vid c:a 1 200°. I närvaro av SiO_2 eller Fe_2O_3 sker emellertid sönderfallet vid något lägre temperaturer (4) under samtidig uppkomst av silikater och ferriter.

Radmann åstadkom vid sitt här tidigare nämnda förfaringssätt sulfatbildning genom att till det kaliförande mineralet sätta gips i ganska stora kvantiteter, något som åtminstone för svenska förhållanden saknar intresse, enär gips ej finnes som naturtillgång. Som nyss anfört kan emellertid kalcium-

sulfat bildas genom en pulverreaktion mellan kalk och svavelkis. Den senare finnes i viss utsträckning i skifferaskan. I händelse av för liten halt tillsättes till önskad mängd FeS_2 i form av finfördelad flotationskis. Någon annan inblandning än $CaCO_3$ har ej förekommit. Försöken ha utförts med Berghaska i luftström, då enligt ovan anförda formler riklig syretillförsel är nödvändig.

Utbytets beroende av inblandningen och upphettningsbetingelserna.

De första orienterande försöken visade en ytterst markerad temperaturkänslighet med hänsyn till utbytet, och det fastställdes, att hela massan måste hållas inom ett snävt område strax under en temperatur, som man lämpligast torde böra benämna kägelsmältpunkten.[1] Denna återigen varierade starkt med kalktillsatsen, som vid stegring höjde temperaturen ifråga.

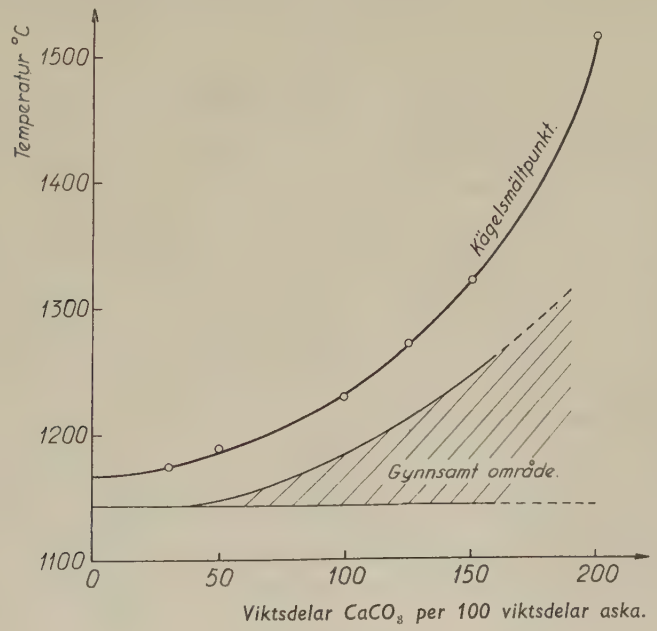

Fig. 3.

[1] Små käglor av massan tillverkades, och deras deformering vid stigande temperatur observerades på vid keramiska prov övligt sätt.

Förhållandena åskådliggöras av Fig. 3, som samtidigt anger det för reaktionen gynnsamma temperaturområdet. Som av figuren framgår kunna olika mängder $CaCO_3$ inblandas. Försök utvisa, att det är från utbytessynpunkt önskvärt att ej använda mindre mängder än 100 g $CaCO_3$ per 100 g aska. Tabell 2 visar utbytenas variation med upphettningsbetingelserna.

Tabell 2.

Blandning	Reaktions-temp. °C	Tid i min.	Utvunnet kali i % av teor.		Konsistens
			lösligt	totalt (lösl. + avrykt)	
100 $CaCO_3$: 100 aska	1 100	60	0	9	osintrad
»	1 120	»	»	6	»
»	1 145	»	45	62	lätt sintrad
»	»	30	34	56	»
»	1 170	60	52	65	»
»	1 190	»	43	59	halvsmält
»	1 240	30	0	22	smält
150 $CaCO_3$: 100 aska	1 200	»	63	73	hårt sintrad

En förupphettning vid temperaturer för svavelkisens sönderdelning synes ej hava nämnvärt inflytande på utbytet. En ökning av $CaCO_3$ tillåter i enlighet med fig. 3 under bibehållet gott utbyte (eller t. o. m. ökat) en stegring av temperaturen.

För hög omsättningsgrad är uppenbarligen det sintrade men osmälta tillståndet en nödvändig förutsättning.

Utbytet kan på grund av askans ringa kishalt ytterligare något förbättras genom omsorgsfull inblandning av flotationskis (Boliden). Med blandningar av 100 del. $CaCO_3$ + 10 del. FeS_2 + 100 del. aska erhölls således redan efter 30 minuter ett utbyte av c:a 70 % lösligt kali vid en temperatur av 1 145°.

Autoklavmetoden.

En behandling av kaliförande bergarter, mineral eller liknande råmaterial, med tryckånga är naturligtvis länge känd

och innebär egentligen intet annat än ett påskyndande av naturens egen vittringsprocess. Rikligt med försök att kombinera vattenångans angrepp med en dekomposition genom inblandningar ha även företagits. I detta sammanhang är särskilt den av Ross (5) angivna metoden att märka. I detta liksom i samtliga andra prövade fall gäller emellertid, att det på grund av råmaterialets individualitet är nödvändigt att utexperimentera speciella kombinationer av reaktionsfaktorerna.

Det visade sig givetvis då först, att det i detta fall icke duger att blanda in $CaCO_3$. Kalkstenen måste först brännas och sedan tillsättas i form av CaO eller $Ca[OH]_2$. De variabla betingelserna utgöras således av proportionen kalk, vattenångans tryck (temp.) och inverkningstid. Därtill visade sig snart komma ett avsevärt inflytande av, om blandningen kalk + aska insattes torr eller fuktig i autoklaven.

I följande Tab. 3 ha några typiska resultat av gjorda försök i laboratorieskala sammanställts.

Tabell 3.

Blandning	Torr el. fuktig	Reaktionstid i t:ar	Tryck atö	Utbyte i % av teor.
50 CaO—100 aska . .	torr —	2	12	2
» . .	» —	4	»	27
» . .	» —	8	»	35
75 CaO—100 aska . .	» —	2	»	5
» . .	» —	4	»	34
» . .	» —	8	»	36
100 CaO—100 aska . .	» —	2	»	12
» . .	» —	4	»	46
50 CaO—100 aska . .	— fuktig	8	»	38
75 CaO—100 aska . .	— »	»	»	51
100 CaO—100 aska . .	— »	»	»	66
75 CaO—100 aska . .	— »	»	20	78
100 CaO—100 aska . .	— »	»	»	84

Av tabellen framgår tydligt att ökning såväl av kalkinblandningen som av reaktionstiden och ångtrycket är mycket för-

månlig. Dessutom ernås högst avsevärda förbättringar, om blandningen insättes i autoklaven i väl fuktat tillstånd. Försök utförda i något större skala vid Kinnekulleverken under förhållanden, där trycket sannolikt varit något över 20 atö och tiden var något längre, gåvo i själva verket nästan 100 %-igt utbyte.

Tekniska synpunkter.

De tre förfaringssätt som laboratoriemässigt utarbetats, *koksaltmetoden*, *svavelkismetoden* och *autoklavmetoden*, kunna kännetecknas på följande sätt, varvid de för utförandet gynnsammaste betingelserna angivits:

Enligt koksaltmetoden upphettas kalihaltiga råmaterial, t. ex. skifferaska, med kalksten och koksalt. Upphettningen sker till omkring 900°, varvid kalium och natrium byta plats, så att 80—90 % av råvarans kalium överföres till kaliumklorid, medan motsvarande mängd natrium ingår i den vattenolösliga delen av reaktionsmassan.

Enligt svavelkismetoden blandas 100 delar skifferaska med 100 delar kalksten och 5 delar svavelkis. Upphettning sker till 1 150—1 200°, då massan sammansintrar. Svavlet i kisen bildar kaliumsulfat, som kan utlakas, och utbytet blir omkring 70 %. Som råvara kan endast utbränd skifferaska (Berghaska) användas, enär svavlet ej oxideras om man använder skiffer eller skifferkoks.

Enligt autoklavmetoden blandas 100 delar skifferaska med 100 delar bränd kalk, varefter upphettning sker med ånga i autoklav vid 12—20 atm. övertryck. Utbytet kan bli fullständigt eller nära fullständigt. Kalit kan dels erhållas som kaliumhydrat, som med rökgaser kan överföras till kaliumkarbonat, dels, om skifferaskan är svavelhaltig, som svavelföreningar, som vid lösningarnas indunstning kunna överföras till kaliumsulfat.

Vid granskning av ovanstående metoders värde ur ekonomisk-teknisk synpunkt är det av intresse att jämföra priserna för olika kalisalter i fredstid. År 1939 kostade 1 ton rent kali (K_2O) som klorid kr. 265: —, som sulfat kr. 400: — och som karbonat kr. 1 010: —. Det föreligger sålunda en betydande skillnad mellan priserna per ton rent kali alltefter den

form i vilken det förekommer. Som karbonat kan det inte direkt användas som gödselmedel men väl som sulfat och klorid. Vissa växter tåla ej större kvantiteter klor, och i dylika fall användes kaliumsulfat som gödselmedel. Man kan dock ej inom landet påräkna högre pris för sulfatet än för kloriden, enär kaliumsulfat ej användes i så stor utsträckning som gödselmedel. Man kan emellertid tänka sig en tillverkning av kaliumkarbonat i fredstid för inhemsk förbrukning och för export. Den inhemska konsumtionen av kaliumkarbonat uppgår till omkring 2 000 ton årligen. Eventuellt kan även kaliumhydrat tillverkas. I avspärrningstider skulle man av karbonatet medelst svavelsyra kunna framställa ett gödselmedel.

Till de båda första förfaringssätten åtgår kalksten och till det tredje bränd kalk. Eftersom utvinningen av kali i första rummet tänkes baserad på alunskiffer, skifferaska eller skifferkoks är det av stor betydelse att kalk rikligt förekommer på samma lokaliteter som skiffern. Vid skifferbrytningen erhålles kalksten i form av orsten som avfall. Orstenen består av stora kalkstensbollar, innehållande förorening av skiffer. Vidare finnes lager av ortocerkalk omedelbart ovanpå alunskiffern. Man har sålunda betydande mängder kalk att tillgå för billigt pris vid skifferoljeverken.

För alla tre förfaringssätten erfordras vidare värme, nämligen vid koksaltmetoden för reaktionsmassans upphettning till 900°, vid svavelkismetoden för reaktionsmassans upphettning till c:a 1 200° och vid autoklavmetoden för bränning av kalksten och alstring av ånga. I alla tre fallen erhålles en reaktionsmassa, som skall utlakas, varefter den erhållna lösningen skall indunstas. Även härtill åtgår värme.

De svårigheter som vidlåda koksaltmetoden bestå i att man såväl vid lakningen av reaktionsmassan som i det förflyktigade saltet erhåller en blandning av KCl och NaCl. Detta gör att den saltmängd som skall utlakas blir betydligt större än produkten, och man måste sedan genom kristallisation skilja de båda salterna från varandra.

Svavelkismetoden medför betydande anläggningskostnader för de roterugnar i vilka reaktionsmassan skall upphettas och torde därför trots sin enkelhet endast i andra hand kunna komma i fråga.

Ekonomiska beräkningar, som utförts med ledning av produktvärde, råvarukostnad och bränsleförbrukning, ha visat att autoklavmetoden är den, som har de största utsikterna att ekonomiskt kunna genomföras. Denna metod erbjuder också den stora fördelen att man efter behag kan få fram olika kalisalter. Genom att utföra indunstningen av lakningslutarna utan lufttillträde eller vid slutindunstning i roterugn i reducerande atmosfär torde allt eller nästan allt kali kunna erhållas som karbonat, vilket är en stor fördel, då detta är det värdefullaste kalisaltet av de här ifrågakommande. Att sedermera vid behov överföra kaliumkarbonatet till sulfat möter inga svårigheter, enär svavelsyra i erforderliga kvantiteter torde kunna framställas. Kaliumkarbonatet skulle vidare under normala förhållanden i viss utsträckning kunna användas till uppslutning av apatit och annat råfosfat enligt Wiborghs förfarande. Vidare är det tänkbart att använda kaliumkarbonatet till framställning av kaliumnitrat, varvid tillverkningen blir analog med tillverkningen av kalksalpeter. Kaliumnitrat eller kalisalpeter torde utblandat med koksalt kunna ersätta chilesalpeter och dessutom ha värde som kaligödselmedel. Om man under normala förhållanden vill överföra en del av produktionen i sulfat skulle man kunna importera gips och omsätta denna med kaliumkarbonatet till sulfat.

Den viktigaste tekniska fråga, som uppstår i samband med kaliutvinning enligt autoklavförfarandet, är på vad sätt man billigast skall kunna få bränd kalk. Förfarandets räntabilitet beror i hög grad på hur denna fråga kan besvaras.

När man har kalksten och skiffer på samma lokaler och erhåller orstenskalk och skifferkoks som avfall eller biprodukter vid skifferoljeframställning, ligger det nära till hands att försöka bränna denna kalk med skiffer eller skifferkoks. Det har länge varit bekant att man i fältugnar, som utgöras av i berget insprängda eller av sten uppmurade schakt, kan bränna kalk med skiffer. Även i schaktugnar sker bränning med skiffer. På samma sätt borde man kunna bränna kalk även med skifferkoks.

Försök utförda med bränning av kalk med skifferkoks i kalkugnar ha dock lämnat ett mindre gott resultat, varjämte arbetskostnaden i omekaniserade ugnar visat sig för dyr.

Det har därför av oss föreslagits att kalkstenen, nedkrossad till 5 mm eller mindre, skulle blandas med det likaledes nedkrossade bränslet, skiffer eller skifferkoks, varefter materialet skulle brännas i en mekaniserad sintringsanläggning av den typ som användes för sammansintring av malmer.

Försök härmed äro redan utförda i halvstor skala och ha givit mycket gott resultat. Det har visat sig att man kan bränna kalkstenen, både ortocerkalk och orstenskalk, såväl med skiffer som med skifferkoks. Utdrivningen av kolsyran blir nästan fullständig, och blandningen av CaO och aska närmar sig förhållandet 50 : 50, så som det bör vara för att kalit skall kunna effektivt utlösas vid den efterföljande ångbehandlingen.

Vid de försök som utförts behandlades den erhållna produkten med ånga av 20 atö i autoklav under 8 timmar, och halten av vattenlösligt kali bestämdes. Man erhöll härvid praktiskt taget allt kali, som fanns i skiffern resp. skifferkoksen i löslig utlakbar form. Om orstenskalk användes synes dock den kvantitet kali som finnes i denna i huvudsak medfölja förbränningsgaserna men bör kunna återvinnas ur dessa.

Härmed synes det måhända viktigaste tekniska problemet vara löst. Sintringsapparaturen är i samband med sintring av malmer numera utarbetad så, att fyllning och tömning av sintringspannorna kan ske helt automatiskt. Med en relativt liten anläggning kan man åstadkomma stor daglig produktion. Man kan därför beräkna att erhålla den för reaktionen nödvändiga blandningen av bränd kalk och aska synnerligen billigt.

Framställningen av kaliprodukter synes dock inte vara ekonomiskt bunden vid utvinningen av skifferolja. Man kan tänka sig en separat brytning av ortocerkalk och skiffer, och då detta kan ske i dagbrott under mycket gynnsamma förhållanden, erhålles såväl kalkstenen som skiffern till mycket billigt pris. Användes skiffer som råmaterial, kan man därtill erhålla vissa kvantiteter olja som biprodukt, enär denna utdrives vid upphettningen i sintringspannan och medföljer förbränningsgaserna.

Sedan man genom sintringsförfarandet erhållit en blandning av bränd kalk och skifferaska blir tillverkningssättet följande. Reaktionsmassan pulveriseras och utröres med vatten,

varefter den ångbehandlas, helst med ett tryck av omkring 20 atm. Härvid överföres kalit väsentligen i vattenlöslig form. Sedan massan uttagits ur autoklaverna utlakas den, varvid erhålles kaliumhydrat och kaliumsvavelföreningar. Lösningen indunstas, och produkten kan genom tillförsel av kolsyra helt eller delvis överföras till kaliumkarbonat.

Beträffande autoklavbehandlingen torde denna fabrikstekniskt komma att ske på liknande sätt som vid framställning av gasbetong. Den pulveriserade och med vatten utrörda reaktionsmassan hälles i lådor, som ställas på vagnar. Tågsätt av dessa vagnar inköras i rörformiga tryckpannor, där ångbehandlingen sker. Det har visat sig att man måste tillsätta så mycket vatten att reaktionsmassan är mer eller mindre flytande före ångbehandlingen. Man har alltså inte möjlighet att av massan göra stycken eller bollar, vilket skulle underlätta fyllning och tömning av tryckpannorna. Det är vidare funnet, att om man utför bränningen vid relativt hög temperatur blir massan inte hård genom ångbehandlingen i autoklaven utan kan lättare avlägsnas ur lådorna.

Denna del av processen skall nu undersökas i halvstor skala. För detta ändamål har medel ställts till förfogande av statsverket, och en försöksanläggning är under uppförande vid Svenska Skifferolje A.-B.s anläggning i Kvarntorp. Vidare skall vid denna anläggning den tekniska uttvättningen av det lösliga kalit ur reaktionsmassan undersökas. Ju starkare lösningar man kan erhålla desto mindre kostar den efterföljande indunstningen. Det lönar sig därför att omsorgsfullt studera även detta problem, varav metodens lönsamhet kan komma att bero. Ur det råmaterial, som finnes i Kvarntorp, erhålles efter kalkbränningen en reaktionsmassa med en kalihalt av 2,5 % i utlösbar form. För att kunna få relativt starka lösningar måste därför en fraktionerad tvättning verkställas.

Först när dessa försök slutförts är det möjligt att uttala sig om metodens lönsamhet i fredstid. Svårigheten härvidlag synes ligga i de stora massor rågods som måste brännas, malas, ångbehandlas och utlakas. För en tillverkning av exempelvis 12 000 ton rent kali per år eller 40 ton per dag åtgår dagligen omkring 3 000 ton råvara, kalkstenen inberäknad. Det blir därför nödvändigt att utbilda sådana processer, som låta

sig till det yttersta mekaniseras. I fråga om kalkbränningen har detta problem emellertid redan lösts.

Så mycket torde emellertid nu (maj 1944) kunna sägas att framställningen av den kvantitet kaliumkarbonat (pottaska) som förbrukas inom landet bör kunna ske med vinst enligt metoden antingen oljetillverkningen pågår eller ej. En dylik anläggning skulle sedan i händelse av avspärrning kunna utvidgas. Ett positivt resultat av de nu pågående försöken bör resultera i att en sådan anläggning projekteras och utföres, närmast i anslutning till ett av skifferoljeverken, och man får av dess drift sedermera möjlighet att bedöma frågan om en tillverkning av kalihaltiga gödselmedel under normala förhållanden blir lönande eller ej.

Sedan denna reservation gjorts beträffande möjligheterna till ett ekonomiskt utförande av metoden under fredstid torde det kunna sägas att några tekniska svårigheter i övrigt inte kunna förväntas uppstå. Med den obegränsade tillgång av råvara som finnes skulle vid total avspärrning nödiga kvantiteter kaligödselmedel kunna framställas enligt autoklavmetoden, och det mål har sålunda uppnåtts som i första hand blivit satt för denna undersökning.

Summary.

During the war apatite concentrates from Swedish iron ore have been recovered in such quantities that the manufacture of phosphate fertilizers is about 70 per cent of the maximum pre-war production. Of nitrogenous fertilizers about 70 per cent of the present consumption can be produced by Swedish works after some extension. The quantities of potash necessary have been imported, but if this import should stop, Swedish agriculture would be entirely without this important plant nutrient. We have therefore once more taken up the old problem of manufacturing soluble potassium salts from Swedish raw materials.

Since experiments had shown that the recovery of potash from cement furnace flue gas was impossible, because the wet method used does not favour an evaporation of potash, the authors investigated the possibility of treating other raw ma-

terials. The potash-bearing residue from alum slate after its pyrolysis to give shale oil is the cheapest raw material available. It contains 4—5 per cent K_2O. We also kept in mind the possible use of feldspars, mica or leptite. It was evident from studying the patent literature that the experimental work should not aim at finding methods based on new principles but that some existing method should be changed and adapted to the materials available.

Laboratory work gave as result three methods, which could be used for raw alum slate, slate ash or slate coke. We have called these methods "the common salt method", "the iron pyrites method" and "the autoclave method".

In the common salt method potash-bearing raw materials, e. g. slate ash, are heated to about 900° C with limestone and common salt. Sodium and potassium change place, 80—90 per cent of the potash in the raw material is converted to potassium chloride, and an equivalent quantity of sodium enters the water-insoluble part of the reaction mass.

In the iron pyrites method 100 parts of slate ash are mixed with 100 parts of limestone and 5 parts of iron pyrites. The mixture is heated to 1 150—1 200° C, when it sinters. The sulphur in the iron pyrites forms potassium sulphate, which can be dissolved in water, and the yield is about 70 per cent. As raw material only slate ash can be employed as the sulphur is not oxidized if slate or slate coke is used.

In the autoclave method 100 parts of slate ash are mixed with 100 parts of quicklime and the mixture is heated in an autoclave in steam at a pressure of 12—20 kg per sq. cm. The yield is almost theoretical. The potash can be obtained as potassium hydroxide, which can be converted to carbonate by flue gas, or if the ash contains sulphur as sulphur compounds, which on evaporation yield potassium sulphate.

Economic calculations have been made and have given the result that the autoclave method seems to be the most promising. Limestone and alum slate occur in the same localities in Sweden and in the manufacture of shale oil there are obtained as by-products both limestone and slate coke of 1 200—1 400 kg cal per kg slate. One of the more important problems is how this thermal value of the slate coke should be employed

in the burning of the limestone. This can be effected by the use of sintering pans. Limestone and slate are crushed to below $^1/_4''$ and a mixture of them is introduced into the sintering pan and ignited, air being drawn through. In this way a mixture of quicklime and slate ash in the correct proportions can be produced, and after pulverizing, mixing with water, and steam-treatment, the potash of the slate ash is recovered as water-soluble compounds. The steam-treated mixture contains only 2.5 per cent of potash and consequently the lixiviation must be arranged rationally.

The methods are now being tested on a semi-industrial scale. Until the results of this work are ready, nothing can be safely said about the financial factor. It can, however, already (May 1944) be predicted that under normal conditions the manufacture of potash would be profitable. The unlimited supply of raw materials should make Sweden independent of importation and safeguard the supply of potash fertilizer during a blockade.

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Optically Active Organic Molecules in Crystal Lattices.

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More than fifteen years ago Reis (1, 2) used space-group data from some crystals containing optically active molecules for the determination of the symmetry of these molecules in the lattice. The enormous increase in the experimental material since then has induced the present author to make the following survey, which also includes discussions of some other problems connected with structures containing optically active molecules.

Optical Activity and Molecular Symmetry.

Pasteur (3) stated that a molecule is optically active if it has such a configuration that it cannot be brought (by rotations and translations alone) to coincide with its mirror image. This is a correct and very convenient statement of the necessary and sufficient condition for a molecule to be optically active. This condition implies that the molecule must not contain a centre of symmetry ($\bar{1}$), a reflexion plane (m) or a four-fold axis of rotatory inversion ($\bar{4}$).[1] Its symmetry may then correspond to one of the 11 point symmetries C_1, C_2, D_2, C_4, D_4, C_3, D_3, C_6, D_6, T, and O. Considering frequent statements in textbooks of organic chemistry, it seems not unnecessary to point out that a lack of all elements of symmetry (i. e. molecular asymmetry, denoted by C_1) is not a necessary condition for optical activity. Nor is the lack of centre of symmetry and

[1] The elements of symmetry are here denoted by the symbols used in the International Tables for the Determination of Crystal Structures (Berlin 1935). Glide reflexion planes are generally denoted by c. In order to save space the crystal classes (point symmetries) and space-groups are denoted by the Schoenflies symbols.

reflexion plane a sufficient condition, as is shown by the fact that a molecule with the symmetry S_4 (possessing an axis $\bar{4}$ as the only element of symmetry) can be brought to coincide with its mirror image and, consequently, cannot be optically active.

In the absence of any better term, molecules, which in a crystal lattice show a symmetry belonging to any of the above 11 point symmetries, are in the following discussion termed optically active molecules. The term is used independently of the fact that the molecule when entering a liquid phase may acquire a higher symmetry, thus giving an optically inactive solution or melt. It is also in this sense that the term optically active has been used in the title of this paper.

Determination of the Molecular Symmetry.

When the space-group and the position of a molecule centre are known the minimum symmetry of the molecule can be stated. The geometrical configuration of the molecule may show a higher symmetry, but as the symmetry of its surroundings is equal to the said minimum symmetry, it seems extremely probable that the latter represents the real molecular symmetry. This implies the assumption that the symmetry of the surroundings is impressed on the forces within the molecule even in cases where this impression has not been found in the geometrical configuration of the molecule itself.

The literature shows many cases where conclusions as to molecular symmetry are not sufficiently founded. The most common error is the assumption that all molecules of the same sort are structurally equivalent. In this way Schneider (4), who found that mesotartaric acid belongs to the space-group C_i^1 with two molecules per cell, concluded that the molecules were asymmetrical (symmetry C_1) although it is not permissible to exclude the possibility of two non-equivalent molecules per cell, each with the symmetry C_i. Frequently, however, a certain symmetry can be proved because the other point symmetries of the space-group are obviously impossible. This may be shown by another example from the space-group C_i^1. Reis (1) concluded that malonic acid, which belongs to this space-group and has two molecules per cell, must have the symmetry C_1,

because the remaining point symmetry C_i would require a highly improbable centro-symmetrical arrangement around the central C atom.

In several cases the mere assignment of a substance to a space-group is sufficient to show that its molecules must possess a symmetry requiring optical activity. In the first place this is the case for all the 65 space-groups lacking $\bar{1}$, m, c, and $\bar{4}$ (i.e. the space-groups belonging to one of the 11 classes lacking $\bar{1}$, m, and $\bar{4}$, namely C_1, C_2, D_2, C_4, D_4, C_3, D_3, C_6, D_6, T, and O). In these space-groups all equivalent molecules are of the same kind, either right-handed or left-handed molecules. Further there are 20 space-groups lacking $\bar{1}$, m, and $\bar{4}$ but possessing c, in which all molecules must be optically active. They are C_s^2, C_s^4, C_{2v}^3, C_{2v}^5, C_{2v}^6, C_{2v}^8, C_{2v}^9, C_{2v}^{10}, C_{2v}^{13}, C_{2v}^{17}, C_{2v}^{19}, C_{2v}^{21}, C_{4v}^5, C_{4v}^6, C_{4v}^8, C_{4v}^{12}, C_{3v}^3, C_{3v}^4, C_{3v}^6, and C_{6v}^2. Here the glide planes c cause the simultaneous appearance of two kinds of equivalent molecules, right-handed and left-handed molecules.

In space-groups where centres of symmetry are the only elements of point symmetry, molecules must occupy general positions and, consequently, be asymmetrical if there are more molecules than centres of symmetry per cell. This is the case in the space-groups C_1^1, C_{2h}^5, and D_{2h}^{15} if the cell contains more than 8 molecules.

The following discussion is based on space-group data which have been exclusively taken from the *Strukturbericht*, Vol. 1—7. The abstracts of works on organic substances have been considered, and all cases have been listed where the existence of optically active molecules, in the sense mentioned above, can be proved. The restriction to organic substances has no other reason than the fact that most substances known to be optically active in solution belong to this class. As a result, optically active molecules have been found in 173 cases.[1]

[1] All chemically related substances which can without any doubt be considered as isomorphous are counted as one case. The number of substances for which optically active molecules have been found is thus greater than 173.

Lattices Containing either Right-handed or Left-handed Molecules.

As has already been mentioned, all equivalent molecules in a lattice belonging to one of the 65 space-groups lacking $\bar{1}$, m, c, and $\bar{4}$ are of the same kind, either right-handed or left-handed molecules. Of the 173 cases of organic crystals with optically active molecules, 94 correspond to lattices of this sort. In 79 of these 94 cases the molecules are known to be optically active in solution. The distribution of the 94 cases over different space-groups can be seen from Table 1.

Table 1. The Distribution over Different Space-groups of Structures with either Right- or Left-handed Molecules.

Space-group	Number of cases		
	Molecules optically active in solution	Molecules optically inactive in solution	Total
C_1^1	2	—	2
C_2^1	1	—	1
C_2^2	23	—	23
D_2^1	2	—	2
D_2^2	3	—	3
D_2^3	6	—	6
D_2^4	36	6	42
D_2^5	1	—	1
$C_4^2 = C_4^4$	—	1	1
C_4^5	—	1	1
$D_4^3 = D_4^7$	2	—	2
$D_4^4 = D_4^8$	1	1	2
D_4^6	—	1	1
$D_3^4 = D_3^6$	1	1	2
$C_6^2 = C_6^3$	—	2	2
C_6^6	—	1	1
$D_6^2 = D_6^3$	1	—	1
$D_6^4 = D_6^5$	—	1	1
	79	15	94

Here, 25 space-groups are represented. Very striking is the high frequency of the space-groups C_2^2 and D_2^4 for lattices of molecules which are known to be optically active in solution. In view of the small number of cases in the third column it is hard to say whether there are any significant differences between the distributions in the second and third columns. A common feature, however, is the frequency of D_2^4.

It is not easy to explain the high frequency of C_2^2 and D_2^4, but it must be pointed out that among the 65 space-groups which permit either right-handed or left-handed molecules, these two are the only ones which contain a digonal screw axis 2_1 as the only sort of symmetry axis. It may therefore be that substances containing optically active molecules have a tendency to crystallize in a lattice showing 2_1 but no other sort of symmetry axis.

Recently, NOWACKI (5, 6) has pointed out the frequency with which the space-groups C_2^2, C_{2h}^5 and D_2^4 are represented by organic crystals. Of 921 organic substances, 12 per cent represented C_2^2, 22 per cent represented C_{2h}^5, and 10.5 per cent represented D_2^4 while never more than 3.5 per cent represented any other space-group. These results are based on all space-group statements in the *Strukturbericht* and are, therefore, not directly comparable with the figures in this paper, which only represent structures where certain molecular symmetries can be proved. NOWACKI's results are, however, certainly influenced by the great number of space-group determinations which have been made on crystals containing optically active molecules (e. g. COX's extensive studies on the sugars and glucosides). This must contribute to the fact that NOWACKI finds a very high frequency for the space-groups which are found in this paper to be most frequent among crystals containing optically active molecules (as will be seen later, C_{2h}^5 is the most frequent space-group among the racemic compounds).

NOWACKI states that the space-groups C_2^2, C_{2h}^5, and D_2^4 are distinguished by the following properties: 1) primitive translation group, 2) asymmorphic space-group, 3) 2_1, c, and $\bar{1}$ as only symmetry elements, 4) 2_1 at right angles to c. These conditions lead exclusively to the above three space-groups but they can naturally not be regarded as the *causes* of the high frequency of these groups. As a matter of fact a much simpler set of conditions leading exclusively to the same space-groups can be stated, namely: 1) the lattice must contain 2_1 and no other sort of symmetry axes, 2) a reflexion plane m is not permitted, 3) a glide reflexion plane must not be situated parallel to 2_1.

Up to this point no attention has been paid in the discussion to the possibility of the molecules rotating freely in the lattice. In the case of rotation, the rotational symmetry of the molecules will certainly cause a tendency towards a rather high symmetry of the molecular arrangement. This, together with the fact that the shape of right- and left-handed molecules will be the same, will probably result in great similarity between the lattices of two antipodes. It is possible that the opposite directions of rotation will be their only difference, and that they will be found to belong to a crystal class which is not compatible with optically active molecules. The material of the *Strukturbericht* does not show any such inconsistencies. As a matter of fact reliable symmetry data cannot be found for any crystals showing signs of free rotation of optically active molecules. Several camphor derivatives show such indications (27, 28) but frequent phase changes and the fact that the symmetries have not been determined by X-ray methods make reliable conclusions impossible.

Very few complete structure determinations have been made on organic crystals containing either right or left molecules. Determined are the structures of ascorbic acid (7) and α-chitosamine hydrochloride (-bromide) (8), the molecules of which are optically active both in solution and in the crystalline state. Furthermore the structures have been established of iodoform(9) and metaldehyde (10), which are not active in solution. The structure analysis of crystals of the two latter compounds has not revealed a geometrical configuration of the molecules consistent with optical activity.

Racemic Compounds.

In the 165 space-groups containing $\bar{1}$, m, c, or $\bar{4}$, every molecule lacking the symmetry elements $\bar{1}$, m, and 4 (i. e. every "optically active" molecule) corresponds to another molecule which is its mirror image. Right- and left-handed molecules, which must occur in equal numbers, can be brought to coincidence by one or several of the symmetry operations corresponding to the elements $\bar{1}$, m, c, or 4.

The search for lattices containing right- and left-handed

molecules has resulted in the finding of 79 cases. In 13 of these the lattices contain equal amounts of antipodes, known to be optically active in solution. These crystals are true racemic compounds but for the sake of brevity all crystals containing right- and left-handed molecules are thus designated here. The distribution of the 79 cases over different space-groups may be seen in Table 2.

Table 2. The Distribution over Different Space-groups of Racemic Compounds.

Space-group	Number of cases			Elements of symmetry bringing right- and left-handed molecules to coincide	Space-group of corresponding active racemic compound
	Molecules optically active in solution	Molecules optically inactive in solution	Total		
$*C_1^1$	3	3	6	$\bar{1}$	C_1^1
$*C_s^2$	—	2	2	c	C_1^1
$*C_s^4$	—	5	5	c	C_1^1
C_{2h}^4	—	1	1	$\bar{1}+c$	C_2^1
$*C_{2h}^5$	5	33	38	$\bar{1}+c$	C_2^2
C_{2h}^6	1	4	5	$\bar{1}+c$	C_2^3
$*C_{2v}^7$	—	4	4	c	C_2^2
$*C_{2v}^9$	1	4	5	c	C_2^2
D_{2h}^5	—	1	1	$\bar{1}+m+c$	D_2^2
D_{2h}^{13}	—	1	1	$\bar{1}+m+c$	D_2^3
D_{2h}^{14}	1	—	1	$\bar{1}+c$	D_2^3
$*D_{2h}^{15}$	1	4	5	$\bar{1}+c$	D_2^4
D_{2h}^{16}	—	1	1	$\bar{1}+m+c$	D_2^4
C_{3i}^1	—	1	1	$\bar{1}$	C_3^1
C_{3v}^6	—	2	2	c	C_3^4
D_{3d}^4	1	—	1	$\bar{1}+c$	D_3^2
	13	66	79		

It is an assumption of highly probable validity that one must be able to bring the molecules of the two antipodes in a true racemic compound to coincide by means of a symmetry operation. If it were not so the two sorts of molecules could not be designated as right- and left-handed molecules in the crystallographic sense of these words. In point of fact this

assumption must be considered as implying the only feature distinguishing a racemic compound from an ordinary molecular compound 1 : 1. The assumption is supported by the fact that each true racemic compound for which the space-group has been determined, belongs to one of the 165 space-groups mentioned above.

As is seen in Table 2, only 16 of these 165 space-groups are represented in the present material. The high frequency of the space-group C_{2h}^5 is the most striking feature of the table. If, from the 165 possible space-groups, one selects those which do not possess any axis of symmetry other than 2_1 (which does not mean that 2_1 is necessary) and furthermore do not possess any m, one obtains the space-groups marked with an asterisk in the first column of Table 2. As can be seen from the table, these (together with C_{2h}^6) doubtless belong to the space-groups most frequently represented by the racemic compounds. Among these space-groups C_{2h}^5 is preferred, i. e. the only space-group containing 2_1, where no glide reflexion plane is parallel to this axis.

It is very often taken for granted that the right- and left-handed molecules in a racemic compound can be brought to coincide by means of a centre of symmetry (1). This corresponds to the view that the two molecules form a pair in which all forces are compensated as completely as possible. Such pairs can always exist when the lattice contains centres of symmetry and as will be seen from Table 2 this is the event in 61 (12 true racemic compounds + 49 from the third column) cases out of the 79 listed. In 18 (1^1 + 17) cases, however, the lattice does not contain any centre of symmetry and the only element bringing right- and left-handed molecules to coincide is a glide reflexion plane (c). Pairs cannot be distinguished here.

It seems as if *d l*-alanine is the only true racemic compound whose structure has been completely determined (29). The molecules are here linked together by hydrogen bonds into a closely knit three-dimensional framework. The structure may be considered as an array of interconnected chains of molecules extending in one direction. Hydrogen bonds bind these chains

[1] *d l*-alanine (29).

into an array of parallel "tubes", each "tube" involving six chains and each chain being common to three "tubes". Of the racemic compounds listed in the third column of Table 2, 10 have been subjected to complete determinations. In 3 cases the resulting geometrical configuration of the molecules definitely shows the existence of right- and left-handed molecules. This is the case for the β-modification of resorcinol (12), anthraquinone (13), and glycine (14). In β-resorcinol, which belongs to the

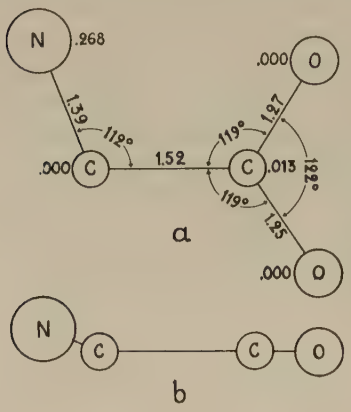

Fig. 1. Glycine molecule (dimensions in Å.) according to (14). *a*. The molecule viewed perpendicularly to a plane containing the two oxygen and the α-carbon atoms. Figures beside the atoms give the heights in Å. of the atomic centres above this plane. The distance of the carboxyl carbon from the plane, 0.013 Å., is below the limit of error. *b*. The molecule viewed perpendicularly to the said plane.

space-group C_{2v}^9, the right- and left-handed molecules are brought to coincide by means of glide reflexion planes. In anthraquinone and glycine they may be brought to coincide by means of centres of symmetry. Fig. 1 shows the shape of the glycine molecule.

The structure determination of glycine (14) has been carried out very carefully and seems to be utterly reliable. The systematic absence of all $h\,0\,l$ reflexions having $h + l$ odd and of odd orders of $0\,k\,0$, definitely establishes the space-group as C_{2h}^5. Considering this, it is remarkable that glycine has been reported to show pyroelectricity (15) and piezoelectricity (16). The pyroelectrical behaviour, however, is stated to indicate the existence of a transition point. Glycine is also known to exist in another modification (17) belonging to the space-group C_s^2 (11) and this modification may, therefore, show pyro- and piezoelectricity. The inoculation experiments, reported by Ostromisslensky (18), are also of great interest as they seem to indicate enantiomorphism.

An investigation, aiming at the explanation of these conflicting data, will be begun in this Institute.

"Active Racemic Compounds".

From a crystallographic point of view it seems unnecessary to make any differentiation between "active racemic compounds" as defined by DELÉPINE (19) and "partial racemic compounds" as defined by FISCHER (20). Both can be derived from a true racemic compound by performing partial changes of the molecules of one antipode. The term "active racemic compound" is often applied to both categories and this practice is followed here.[1]

The term active racemic compound has a meaning only if it implies an essential distinction from an ordinary molecular compound 1 : 1. It seems most practical to require that the active racemic compound be isomorphous with a corresponding true racemic compound. This agrees with the fact that isomorphism with a corresponding true racemic compound has been generally used as a proof of a substance being an active racemic compound (e. g. 19, 22, 23, 24). An active racemic compound is then evidently built up mainly according to the same principles as the corresponding true racemic compound. The unchanged parts of the molecules still occupy the same or nearly the same positions as in the true racemic compound and can be more or less approximately brought to coincide by means of the same symmetry elements, which, in the true racemic compound, bring the right- and left-handed molecules to coincide. In a strict sense, however, these elements have disappeared. On the assumption that no other symmetry changes occur, there will be a fixed relation between the space-group of an active racemic compound and the space-group of a corresponding true racemic compound. The last column of Table 2 contains the space-groups of the active racemic compounds derived under this assumption from true racemic compounds belonging to the space-groups of the first column. It is evident that the space-group C_2^2 must be expected to be very frequent among the active racemic compounds.

It seems quite possible that in certain cases the isomorphism with the true racemic compound may be maintained even if

[1] In order to avoid confusion with one of the earlier terms of limited meaning, FREDGA (21) has suggested "quasi-racemic compound" as a term common to both categories.

one of the antipodes is changed to a molecule which is optically inactive in solution. The latter molecules may then obtain an "optically active" configuration when entering the lattice. Fredga (21), who was the first to discuss the possibility of active racemic compounds of this kind, has provided strong evidence of the existence of such a compound between $\alpha\alpha'$-dimethylglutaric acid and glutaric acid.

Structure or space-group determinations have not yet been carried out on any active racemic compound.

Solid Solutions.

Soon after Kipping and Pope (25) had focussed attention on the so-called pseudo-racemic mixed crystals, it was shown by Roozeboom (26) that these products were to be considered as solid solutions. In spite of the long interval which has elapsed since then, the very interesting crystallographic features of these solutions seem never to have been discussed.

It is sometimes stated that a solid solution between two antipodes can only occur if the crystals of the antipodes are isomorphous. As antipode crystals can never be isomorphous this statement is wrong, but it contains a kernel of truth in so far as it is very difficult to imagine a solid solution between antipodes without assuming conditions which render the crystals nearly isomorphous.

A solid solution between antipodes must be of the substitution type and a substitution of a left-handed for a right-handed molecule or vice versa can only take place if the right-handed and left-handed molecules are rather similar as to their external form and forces. This condition may be expressed by saying that the structure of the molecule must not differ too much from a structure which is identical with its mirror image.

Another condition concerns the symmetry of the molecular arrangement. It does not appear very likely that a right-handed molecule can enter a crystal of the left-handed antipode if the forces from the surrounding molecules are very different from those in the right-handed crystal. Consequently, the surroundings must be rather similar in the two crystals, which

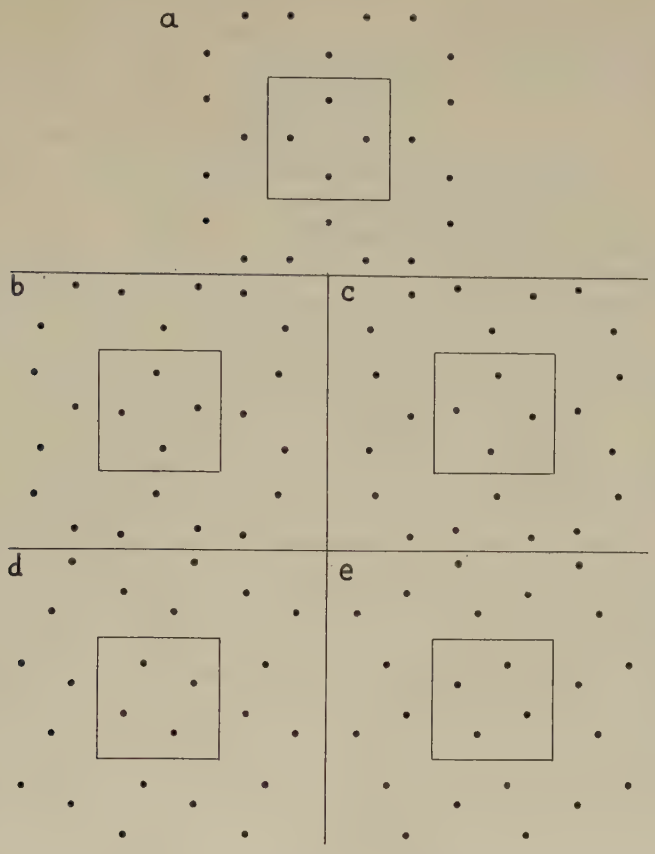

Fig. 2. Distribution of molecular centres in: *a* solid solution 1:1 between two antipodes; *b*—*c* and *d*—*e* two pairs of antipodes with different degrees of deviation from *a*.

implies that the arrangement of the molecules must not differ too much from an arrangement which is identical with its mirror image.

A very schematic two-dimensional illustration is given in Fig. 2, where the molecular centres are represented by black dots without showing the molecular symmetry. 2 *a* represents a molecular arrangement identical with its mirror image, while *b* and *c* represent left- and right-handed arrangements, differing slightly from *a*. *d* and *e* represent another pair of antipodes deviating still more from *a*. If right-handed molecules from *e* enter *d* they acquire very different environments (from a two-

dimensional point of view). In the pair *b*—*c* the environments are more similar and solution is more likely to occur. The solid solution 1 : 1 will be represented by *a*. At this composition the lattice cannot be enantiomorphous. If a complete mutual solubility of *d* and *e* be assumed, the series *d*—*b*—*a*—*c*—*e* may also illustrate the lattice changes in the solid solutions between these components.

In conclusion it may be stated that a probable condition for the mutual solubility of antipodes is that their lattices must not differ too much from a lattice which is identical with its mirror image. The solid solution 1 : 1 will show an increase in symmetry compared with the antipodes.

It has already been mentioned that free rotation of the molecules probably causes the lattices of two antipodes to be very similar. One may, therefore, assume that molecular rotation will favour the formation of solid solutions. Kipping and Pope (25) already found a great many examples of solid solutions among the camphor derivatives. The strong evidence for the frequency of free molecular rotation in crystals belonging to the camphor group (27, 28) is very interesting in this connection. In several cases Kipping and Pope found the crystals of the antipodes and the solid solutions 1 : 1 to have almost identical crystalline forms and melting points. This is exactly what would be expected if molecular rotation were assumed.

The conditions for the solubility of the antipodes in a racemic compound must be the same as the conditions now discussed for the mutual solubility of the antipodes.

It is probable that the right- and left-handed molecules are generally distributed at random in the solid solutions. At compositions corresponding to simple molecular proportions, above all at 50 mol per cent, ordered distributions leading to superstructures may occur, especially when the temperature is lowered. Such a superstructure may or may not be a racemic compound.

It is probable that many of the points discussed here can be elucidated by X-ray investigations. This is especially the

case with the problems related to solid solutions and molecular rotation. An attack on these problems is planned in this Institute.

Summary.

A survey of crystals containing optically active molecules shows that optical antipodes, among the space-groups which permit either right- or left-handed molecules, prefer those (C_2^2 and D_2^4) which possess a digonal screw axis as the only symmetry axis.

Among the space-groups which permit right- and left-handed molecules, the racemic compounds prefer those which do not possess any other axis than a digonal screw axis and furthermore do not possess a reflexion plane. Among these space-groups, C_{2h}^5 is especially preferred.

Racemic compounds exist in which a glide reflexion plane is the only symmetry element bringing right- and left-handed molecules to coincidence. Pairs of right- and left-handed molecules cannot be distinguished here.

A probable condition for the mutual solubility of antipodes is that their lattices must not differ too much from a lattice which is identical with its mirror image. This implies that their lattices must be very similar. Free molecular rotation may facilitate the fulfilment of this condition. The solid solution 1 : 1 will show an increase in symmetry compared with the antipodes.

Lattices containing molecules which in the crystal possess a symmetry compatible with optical activity, but which are optically inactive in solution, have been discussed.

The author wishes to express his thanks to his colleague Professor A. Fredga, for many valuable discussions related to this paper.

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Méthode dilatométrique pour étudier la vitesse de cristallisation de solutions sursaturées de sucre.

(Communication préliminaire).

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Pendant les dernières années, des recherches sur les substances à poids moléculaire élevé qui interviennent dans l'industrie du sucre, ont été exécutées à l'Institut de Chimie-Physique d'Upsal (1, 2, 3). Ces études tendant à devenir de plus en plus étendues, il devenait nécessaire de se spécialiser dans le domaine de ces substances qui, d'une façon ou d'une autre, jouent un rôle important dans les procédés employés par l'industrie sucrière, par exemple dans l'épuration des jus sucrés ou la cristallisation du sucre. Comme première étape dans cette étude de l'importance des colloïdes pour la fabrication du sucre, nous avons commencé à examiner comment la cristallisation est entravée par ces substances.

Nous ne sommes pas encore arrivés à construire un appareil en tout point irréprochable, pour déterminer la vitesse de cristallisation. Les expériences de cristallisation décrites ci-dessous doivent, pour cette raison, être considérées seulement comme des expériences-types préliminaires.

C'est pourquoi je remets à plus tard une discussion complète du problème de la cristallisation, où nous pourrons donner éventuellement des résultats plus définitifs de nos propres expériences.

Parmi les déterminations de vitesse de cristallisation effectuées pour différentes substances, je mentionnerai, seulement en passant, que Marc et ses collaborateurs ont étudié la vitesse de cristallisation, de différents sels par exemple, en variant

les conditions des expériences (4). Marc suivait la cristallisation, en mesurant le pouvoir conducteur de la solution sursaturée à des intervalles appropriés, ou en déterminant le poids sec des solutions.

Je ne donnerai pas non plus une revue générale des travaux qui ont été entrepris pour déterminer la vitesse de cristallisation du sucre à des températures différentes, à des sursaturations différentes, ou en y mêlant différentes impuretés. Je me contente de citer Kucharenko et ses collaborateurs qui ont déterminé la vitesse de cristallisation du sucre, en sortant, à des moments différents, les cristaux de sucre de la solution sursaturée et en les pesant. (Une partie de ces expériences sont publiées dans des revues russes difficilement accessibles). Finalement, je veux signaler que Smolénski et Zélazny ont étudié la cristallisation du sucre, en mesurant la concentration de la solution sursaturée à différents moments à l'aide d'un réfractomètre (5). Parmi les travaux qui traitent la cristallisation du sucre au point de vue théorique, on peut signaler un article de Kucharenko (6).

Pour les expériences que nous avons entreprises, nous avons fait usage d'une méthode dilatométrique, c'est-à-dire que nous avons étudié la marche de la cristallisation, en mesurant la diminution infime de volume qui se produit quand le sucre cristallise dans la solution sursaturée. Les cristaux de sucre ont un poids spécifique un peu plus grand que la solution sursaturée. (Le poids spécifique du sucre à 25° C est égal à 1,5871, tandis q'une solution de sucre par ex. à 70,0 % a un poids spécifique de 1,3445 à la même température.) Autant que je sache, cette possibilité d'étudier la vitesse de cristallisation n'a pas été expérimentée jusqu'alors.

Dans ce but, j'utilise, jusqu'à nouvel ordre, un dilatomètre fait d'un entonnoir séparateur, contenant environ 117 ml (voir Fig. 1). Le tuyau de l'entonnoir a été coupé à cinq centimètres au-dessous du robinet et à sa place un capillaire, long de 25 cm. a été soudé. Le diamètre intérieur du capillaire est de 1,5 mm. A l'extrémité supérieure du capillaire, un tuyau en caoutchouc C d'environ 3 cm. l'emboîte. En outre, on y a soudé un tube latéral muni d'un robinet D. Pour tenir le robinet E dans la bonne position, on a ajouté une pince à

ressort métallique. Le bouchon G est maintenu par trois ressorts en spirale. Le dilatomètre est vissé dans un cadre spécial qui, de son côté, est fixé à l'aide de deux pinces.

L'agitation dans le dilatomètre se fait à l'aide d'un agitateur en métal à ailes pliables. L'agitateur est suspendu à un fil métallique de 0,5 mm. de diamètre qui passe par le capillaire. L'extrémité supérieure du fil est fixée à l'axe d'un petit moteur. (Le moteur n'est pas visible sur la Fig. 1).

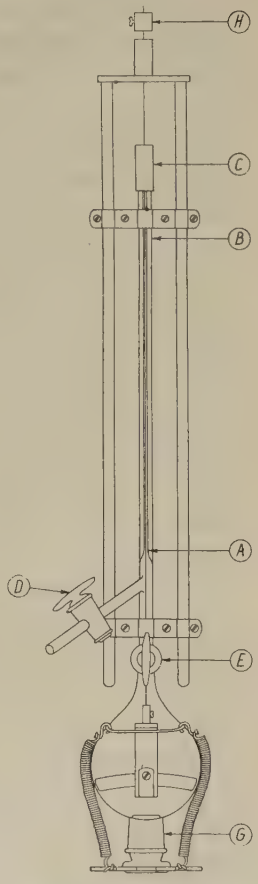

Fig. 1. Dilatomètre pour les expériences de cristallisation.

Il est difficile de dire si l'agitation est effective partout, si elle se produit aussi par exemple dans la partie supérieure de l'appareil. Il est probable que l'on pourrait changer un peu la forme du ballon en verre. Mais si l'on utilise toujours le même nombre de tours pour l'agitateur, les conditions devraient bien être tout-à-fait semblables à chaque expérience.

Pendant l'agitation, il se produit une certaine quantité de chaleur de friction. La température à l'intérieur du dilatomètre est donc un peu plus élevée (bien que de façon infime) que dans l'eau du thermostat, dans lequel le dilatomètre est plongé pendant l'expérience. En construisant un nouveau dilatomètre, on doit par suite le disposer de telle manière qu'il sera possible de mesurer la température également à l'intérieur du dilatomètre. Pour l'appareil dont nous disposons actuellement, nous pouvons cependant évaluer cette augmentation de température en mesurant le changement de volume avant de mettre le moteur en fonction et après l'y avoir mis. De cette façon, la température à l'intérieur du dilatomètre s'est avérée d'environ 0,2° plus haute que la température du thermostat. Pourtant on peut considérer que la température à l'intérieur du dilatomètre a été la même pour chaque expérience, car le nombre

de tours de l'agitateur est resté constant, de sorte qu'on peut admettre que la friction a été approximativement la même à chaque expérience.

Le thermostat dans lequel l'appareil est plongé pendant les expériences, doit naturellement être très sûr, car autrement le dilatomètre fonctionnerait comme un thermomètre très sensible.

De même, la pièce dans laquelle le thermostat est installé, doit être maintenue à la même température que l'eau du thermostat, car on est forcé de sortir l'appareil hors du thermostat pour le remplir avant le commencement de l'expérience.

Au début de l'expérience, on introduit dans le dilatomètre la solution sursaturée ainsi que les cristaux de sucre qui doivent augmenter dans la solution. (Le remplissage de l'appareil est décrit ci-dessous d'une manière plus détaillée). Ensuite on remplit presque tout le capillaire avec de l'huile de paraffine, comme on ne peut pas avoir de solution de sucre sursaturée cristallisant dans le capillaire. On met en fonction l'agitateur, quelques instants plus tard l'équilibre de température s'établit dans l'appareil, et l'on peut lire alors, au moment convenable, la position du ménisque dans le capillaire. Pour la lecture, on n'arrête pas l'agitateur. On lit la position du ménisque en se reportant à une marque dans la partie supérieure du capillaire et l'on considère comme etant positif le mouvement du ménisque, s'il descend dans le capillaire dans la direction du dilatomètre proprement dit. Par conséquent, si, par exemple, le ménisque se déplace de 10,5 mm à 15,0 mm, cela implique une diminution de volume du système dans le dilatomètre.

Avant de décrire le sucre et les solutions de sucre introduits dans le dilatomètre pour les expériences, nous voudrions tout d'abord indiquer la meilleure manière de remplir le dilatomètre.

L'appareil (avec l'agitateur) est d'abord tempéré dans le thermostat. Ensuite on l'enlève, l'essuie, et l'on met une pince pressante sur le tuyau en caoutchouc C. Le robinet D reste fermé. L'appareil est ainsi fermé du côté du tube latéral aussi bien que du côté du capillaire. On renverse l'appareil, enlève le bouchon G et met dans l'appareil d'abord les cristaux de

sucre et ensuite la solution sursaturée. Comme l'appareil est fermé du côté du tube latéral et à l'extrémité du capillaire, la solution visqueuse n'avance pas plus loin que la noix du robinet E. Si des bulles d'air venaient à se former, on tirerait doucement sur le fil de l'agitateur, ou on les ferait partir à l'aide d'un fil métallique. Ensuite, on presse le bouchon G, graissé avec de la vaseline, dans son ouverture, tout en retournant l'appareil au même instant dans sa position normale, et on ouvre le robinet D pour que le bouchon entre complètement. De cette manière, on évite que la solution de sucre n'entre dans le capillaire. On serre comme il faut le bouchon à l'aide de trois ressorts en spirale. On enlève la pince pressante à l'extrémité supérieure du capillaire et on enlève par suction la solution de sucre qui serait entrée éventuellement dans le tube latéral. On laisse s'échapper par le robinet E les bulles d'air qui auraient pu se former dans le dilatomètre. Ensuite on remplit le capillaire par le tube latéral avec de l'huile de paraffine, après cela on ferme le robinet D. Pendant tout le temps où l'on remplit l'appareil, la température de la pièce doit être la même que celle du thermostat. On plonge de nouveau l'appareil dans le thermostat et on attache le fil de l'agitateur à l'axe du moteur. Le dispositif d'arrêt H est placé ensuite convenablement. Le but de ce dispositif d'arrêt est d'empêcher que le lourd agitateur métallique ne puisse tomber et casser le fond du dilatomètre, au cas où le fil se détacherait du moteur.

Les cristaux de sucre, introduits au début des essais, étaient des K 2 tamisés, catégorie de sucre très pure. D'après des indications, la grosseur des grains variait entre 1,2 et 0,83 mm. Dans les expériences suivantes, le poids de ce sucre était toujours exactement de 3 gr., ce qui correspond à environ 3 000 cristaux. Naturellement, si l'on considère séparément les cristaux de sucre, leur poids et leur surface varient, mais nous espérons qu'en choisissant un si grand nombre de cristaux, nous pouvons être sûrs, de façon générale, d'avoir utilisé la même surface de ce sucre K 2. (La vitesse de cristallisation dépend évidemment de la surface des cristaux de sucre).

Quand ces cristaux sont projetés de tous côtés par l'agitateur, on ne peut éviter qu'une partie de ceux-ci ne se casse,

et de ce fait, la surface augmente, et des centres de cristallisation secondaires se forment. Comme cependant le nombre de tours de l'agitateur est approximativement le même à toutes les expériences et que les autres conditions de l'expérience sont identiques à chaque fois, on pourra négliger cet effet, tant qu'il s'agit simplement de comparer les uns aux autres p. ex. les ralentissements de cristallisation produits par différentes substances étrangères. Des expériences ont montré en outre que pour les vitesses d'agitation habituelles, le nombre de tours du moteur n'a pas une influence notable.

La température du thermostat a toujours été de 25,0° C. Nous n'avons pas encore étudié la cristallisation à des températures différentes.

On a varié le degré de sursaturation des solutions de sucre, mais on a surtout employé des solutions contenant 70,0, 69,5 et 69,0 % de sucre. (Selon le tableau de Grut, une solution de sucre saturée à 25,0° C contient 67,68 % de sucre.)

Les solutions ont été préparées en dissolvant le sucre et les impuretés éventuelles à une température plus élevée, dans des bouteilles bien fermées, de sorte que des pertes d'eau étaient exclues. Les solutions ont toujours été plongées dans de l'eau bouillante, pendant une heure, le jour précédant l'expérience, ensuite elles ont été tempérées à 25,0° C jusqu'au jour suivant. Le traitement à chaud des solutions avant les expériences a donc toujours été identique, autant que cela fut possible, pour toutes les expériences décrites ci-dessous.

Jusqu'à présent, les expériences avaient surtout pour but de voir si la méthode était suffisamment sensible pour que l'on pût comparer de cette manière les uns aux autres les ralentissements de vitesse, produits sur la cristallisation par différentes substances étrangères. La plupart des expériences ont été exécutées de façon à examiner la vitesse de cristallisation de solutions contenant 69,5 % de sucre et 0,3 % d'impuretés, en marquant simplement la position du ménisque dans le capillaire en fonction du temps.

Les « impuretés » dans ces expériences-types ont été d'une part des substances qui se présentent réellement en pratique, d'autre part des substances qui pratiquement n'ont aucune importance pour la fabrication du sucre, mais qui offrent un

intérêt de principe pour de telles études sur le ralentissement de la cristallisation.

Sur la Figure 2 sont tracées quelques courbes de cristallisation qui ont été obtenues pour des solutions contenant seulement du sucre et de l'eau. La concentration du sucre a été la suivante:

Exp. No.	% de sucre
K 70	70,0
K 68	69,5
K 67	69,0

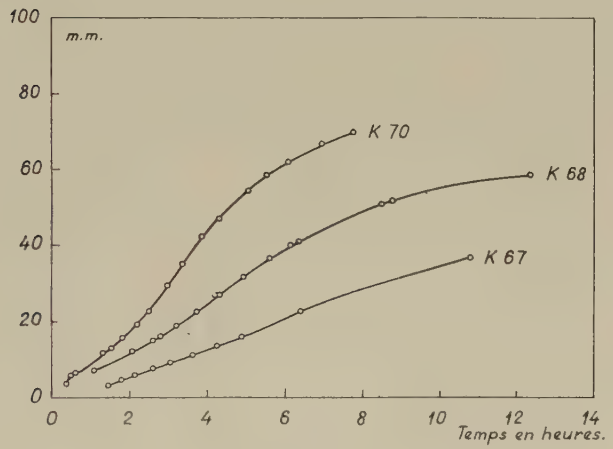

Fig. 2.

Sur le diagramme, la position du ménisque dans le capillaire a été marquée en fonction du temps.

A titre de comparaison, nous donnons ici un calcul du changement de volume qui se produit à la cristallisation de quelques solutions sursaturées de sucre. On a fait usage des valeurs habituelles de tableaux donnant le poids spécifique des cristaux de sucre et des solutions sursaturées de sucre. Pour le calcul, on supposait que 109 ml de solution sursaturée de sucre étaient introduits dans l'appareil, que le diamètre du capillaire était de 1,5 mm et le diamètre du fil de l'agitateur de 0,5 mm, ce qui correspond environ à nos conditions expérimentales. Les calculs ne peuvent être qu'approximatifs, parce que la valeur du poids spécifique des cristaux de sucre en particulier, n'est vraisemblablement pas très sûre.

Si la solution sursaturée se compose de 70,00 % de sucre et de 30,00 % d'eau, on obtient, à l'aide des valeurs des tableaux indiquant les poids spécifiques, un changement de volume de 0,11 ml, quand la solution ce cristallise, jusqu'au moment où la saturation est tout juste atteinte. (D'après le tableau de Grut, une solution saturée de sucre à 25,0° C contient 67,68 % de sucre). Cela correspond à un déplacement du ménisque de 7 cm dans le capillaire. (Comparer avec K 70, Fig. 2).

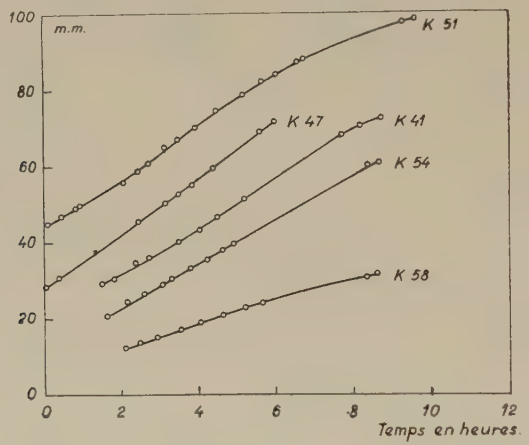

Fig. 3.

Exp. No.	Impureté ajoutée
K 51	éosine
K 47	dextrane
K 41	glucose
K 54	glycine
K 58	pectine de betterave

De même, on obtient pour une solution contenant 69,50 % un changement de volume de 0,08 ml et un changement de la position du ménisque dans le capillaire de 5 cm. (Comparer avec K 68, Fig. 2).

Dans la Fig. 3, on a tracé quelques courbes qui montrent les résultats obtenus en ajoutant différentes substances à la solution de sucre. Les expériences ont été faites avec des solutions contenant 69,5 % de sucre, 0,3 % d'« impuretés » et 30,2 % d'eau. Le tableau suivant montre quelles sortes d'impuretés intervenaient aux différentes expériences.

Exp. No.	Impureté
K 51	éosine
K 47	dextrane
K 41	glucose
K 54	glycine
K 58	pectine de la betterave à sucre.

En considérant l'inclinaison de la courbe, on peut voir directement, sans calculs mathématiques, si une substance ralentit la cristallisation plus fortement qu'une autre. En partant de

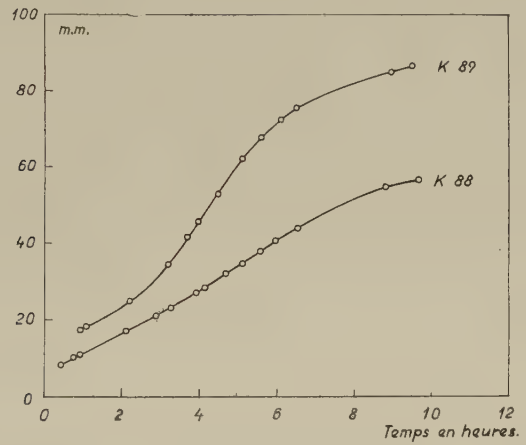

Fig. 4.

ces expériences et de quelques autres, on a pu tirer la conclusion que p. ex. glucose, dextrane, glycine, éosine, gélatine, bétaïne et chlorure de sodium ont une influence très peu marquée sur la cristallisation du sucre. La pectine de betterave à sucre ralentit un peu la vitesse de cristallisation.

Nous avons étudié de même l'influence du violet cristallisé, du bleu de méthylène et d'une dextrine impure sur la vitesse de cristallisation, et nous croyions d'abord que nous avions trouvé là quelques substances qui influençaient fortement la cristallisation. Il se montrait cependant plus tard que ces substances étaient faiblement acides, et qu'elles causaient, pour cette raison, une faible inversion du sucre, ce qui diminuait la sursaturation des solutions. L'amoindrissement de sursaturation avait comme conséquence un ralentissement de cris-

tallisation. Quand on répétait les expériences avec ces substances, mais en y ajoutant un peu de phosphate de soude pour conserver la neutralité de la solution, l'effet disparaissait et la cristallisation progressait normalement.

L'action de ralentissement produit par la pectine de betterave a été examinée de même avec des concentrations plus élevées, de façon à rendre l'effet plus grand. Sur la Fig. 4, la courbe K 88 a été obtenue pour une solution de la composition suivante: 69,5 % de sucre, 0,6 % de pectine de betterave. 29,7 % d'eau, 0,055 % de $NaH^2PO^4 \cdot 1\ H^2O$ et 0,145 % de $Na^2HPO^4 \cdot 12\ H^2O$. A titre de comparaison, on a tracé la courbe K 89, établie pour une solution de même composition que K 88, mais en remplaçant la pectine par du glucose. Le phosphate de soude a été ajouté pour que la solution reste neutre. Comme on pouvait le supposer, l'effet de ralentissement produit dans ce cas est plus grand que dans la Fig. 3.

Des expériences semblables ont montré que le raffinose ralentit la vitesse de cristallisation du sucre. Quand on comparait l'effet du raffinose à celui du glucose, on obtenait des courbes semblables à celles de la Fig. 4.

Résumé.

Nous avons élaboré une méthode dilatométrique pour mesurer la vitesse de cristallisation de solutions sursaturées. Les recherches décrites ci-dessus ont eu surtout pour but d'étudier la vitesse de cristallisation du sucre en présence de différentes « impuretés », mais la méthode peut naturellement être appliquée à d'autres substances que le sucre.

On peut examiner l'action de ralentissement exercée par différentes substances sur la cristallisation, en comparant les inclinaisons des « courbes de cristallisation » obtenues.

Parmi les substances examinées jusqu'à présent, la pectine des betteraves à sucre et le raffinose ont exercé une action de ralentissement sur la cristallisation du sucre.

Nous désirerions exprimer ici notre reconnaissance à Monsieur le Professeur A. Tiselius pour tous ses bons conseils. Quand nous concevions le plan de ce travail, Monsieur O.

Wiklund, Ingénieur à Arlöv, a mis à notre disposition la grande expérience qu'il a en ce domaine.

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Über die Berechnung von Molekulargewichten polymolekularer Substanzen aus Messungen von Sedimentationsgeschwindigkeit und Diffusion.

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Eine grosse Zahl in der Natur vorkommender oder künstlich hergestellter hochmolekularer Substanzen sind polymolekular[1], d. h. man erhält oder gewinnt sie in Form von Mischungen verschieden grosser Moleküle, welche man jedoch alle durch Polymerisation einer gewissen Einheit, des Grundmoleküls, gebildet denken kann. Dies gilt für Cellulose, Cellulosederivate, Kautschuk, Polyvinylderivate etc.

Um eine vollständige Kenntnis der Molekulargewichte derartiger Stoffe zu erhalten, ist es notwendig die Funktion zu kennen, die die prozentuale Verteilung der Molekulargewichte in der vorliegenden Substanz angibt. Im allgemeinen ist jedoch die Verteilungsfunktion unbekannt und da sie unter allen Umständen schwer zu bestimmen ist, muss man sich oft mit einem Molekulargewichts-Mittelwert begnügen. Derartige Mittelwerte können auf eine unbegrenzte Anzahl Arten definiert werden, aber nur drei verschiedene Arten von Molekulargewichtsmitteln haben allgemeine Verbreitung gefunden, nämlich das Zahlenmittel M_n, das Gewichtsmittel M_w und das Z-Mittel M_z[2] (Lansing und Kraemer (2)).

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[1] Man spricht auch von Polydispersität. Für eine Diskussion dieser Begriffe, Polydispersität und Polymolekularität, sei auf eine Arbeit von Schulz (1) verwiesen.

[2] In einer späteren Arbeit von Kraemer (3) wird die Bezeichnung C-Mittel statt Z-Mittel vorgeschlagen.

Die Mittelwerte sind durch folgende Gleichungen definiert:

$$M_n = \frac{\int_0^{c_0} d\,c}{\int_0^{c_0} \frac{1}{M} d\,c} \tag{1}$$

$$M_w = \frac{\int_0^{c_0} M\,d\,c}{\int_0^{c_0} d\,c} \tag{2}$$

$$M_z = \frac{\int_0^{c_0} M^2\,d\,c}{\int_0^{c_0} M\,d\,c} \tag{3}$$

wobei

$$M_n \leq M_w \leq M_z \tag{4}$$

(Das Gleichheitszeichen gilt nur bei Homogenität.)

c_0 bedeutet die Totalkonzentration der Substanz (die man sich gelöst zu denken hat).

Es gibt nur wenig experimentell anwendbare, sicher theoretisch begründete Methoden zur direkten Molekulargewichtsbestimmung. Genannt seien die chemische Molekulargewichtsbestimmung, speziell in der Form der Endgruppenbestimmung, weiter Messung des osmotischen Druckes, Sedimentationsgleichgewicht und schliesslich Kombination von Messungen der Sedimentations- und Diffusionsgeschwindigkeit. Hinsichtlich der Methodik für die Molekulargewichtsbestimmung auf osmotischem Weg sei auf eine zusammenfassende Arbeit von Schulz (4) hingewiesen. Ultrazentrifugierung und Diffusion werden ausführlich in Svedberg und Pedersens Monographie (5) behandelt. Kurze Zusammenfassungen sind an verschiedenen Stellen publiziert, z. B. (6, 7).

Chemische Molekulargewichtsbestimmung und Messungen des osmotischen Druckes geben Zahlenmittel, Sedimentations-

gleichgewichte Gewichts- oder Z-Mittel. Es ist ein bedeutend schwereres Problem, zu bestimmen, was man für einen Mittelwert erhält bei der Kombination von Sedimentationsgeschwindigkeits- und Diffusionsmessungen, und dieser Aufsatz stellt einen ersten Versuch zur Klärung dieser Frage dar.

Es muss hinzugefügt werden, dass die meist verbreitete Relativmethode zur Messung von Molekulargewichten, die auf der Bestimmung der spezifischen Viskosität nach Staudinger beruht, ein Gewichtsmittel gibt, wenn die K_m-konstanten richtig bestimmt sind (8).

Der Berechnung von Molekulargewichten aus Sedimentations- und Diffusionsmessungen liegt Svedbergs Formel (9) zugrunde:

$$M = \frac{R\,T}{1 - V \cdot \varrho} \cdot \frac{s}{D} \tag{5}$$

wo

M = Molekulargewicht.
s = Sedimentationskonstante.
D = Diffusionskonstante.
V = partielles spezifisches Volumen der gelösten Substanz.
ϱ = Dichte der Lösung.[1]
R = Gaskonstante.
T = Abs. Temperatur.

Hinsichtlich der speziellen Verhältnisse, die auftreten können, wenn die hochmolekulare Substanz elektrolytisch dissoziiert ist, siehe Lamm (11).

Zur Bestimmung des Molekulargewichtes ist die Kenntnis dreier Materialkonstanten der untersuchten Substanz nötig, nämlich der Sedimentationskonstante s, der Diffusionskonstante D und des partiellen spezifischen Volumens V. Ist die Substanz polymolekular, so variieren s und D mit dem Molekulargewicht, während V als davon unabhängig betrachtet werden kann. Scholten (12) zeigte, dass dies für Nitrocellulose der Fall ist.

[1] Burgers (10) erachtet doch, dass man die Dichte des Lösungsmittels verwenden sollte. Bei den Molekulargewichtsbestimmungen ist die Frage bedeutungslos, da s und D immer nach der Konzentration Null hin extrapoliert werden.

Da Sedimentations- und Diffusionskonstanten in einer polymerhomologen Reihe eindeutig mit dem Molekulargewicht variieren, kann man sich eine Verteilungsfunktion mit s oder D als Variable anstatt M denken, und man kann folglich auch Zahlen-, Gewichts- und Z-Mittel s_n, s_w und s_z resp. D_n, D_w und D_z durch (1), (2) und (3) analoge Gleichungen definieren. Die so nach Gleichung (5) berechneten Molekulargewichte bezeichnen wir mit doppelten Indices, wo der erste Index den für s verwendeten Mittelwert und der zweite den für D verwendeten bezeichnet, z. B.

$$M_{n,w} = \frac{R\,T}{1 - V \cdot \varrho} \cdot \frac{s_n}{D_w} \tag{6}$$

Bestimmt man Sedimentations- und Diffusionskonstanten s_w resp. D_w, so kann man versucht sein zu glauben, dass das Einsetzen der Werte in (5) M_w gäbe. Es ist jedoch leicht zu zeigen, dass dies nicht der Fall ist. Früheren Definitionen zufolge findet man nämlich

$$M_w = \frac{R\,T}{1 - V \cdot \varrho} \cdot \frac{\int_0^{c_0} \frac{s}{D}\,dc}{\int_0^{c_0} dc} \tag{7}$$

während andererseits

$$M_{w,w} = \frac{R\,T}{1 - V \cdot \varrho} \cdot \frac{\int_0^{c_0} s \cdot dc}{\int_0^{c_0} D \cdot dc}. \tag{8}$$

Nur für den experimentell nicht realisierten Fall, wo $D = \text{konst.}$, sind M_w und $M_{w,w}$ identisch.

Aus obigem geht hervor, dass das vorliegende Problem in drei Teile aufgeteilt werden kann:

1. Bestimmung der Art des Mittelwerts, den die experimentelle Bestimmung von D liefert.
2. Bestimmung der Art des Mittelwerts, den die experimentelle Bestimmung von s liefert.
3. Bestimmung des Molekulargewichts-Mittelwerts, den man aus gegebenen Mittelwerten von s und D erhält.

Diffusionsmessung.

Die Frage der Mittelwerte bei der Diffusion polymolekularer Systeme ist von Gralén (13, 14) ausführlich behandelt worden für den Fall, dass man bei den Experimenten die Lamm'sche Skalenmethode (15) verwendet. Durch verschiedenartige Ausführung der Berechnung kann man eine theoretisch unbegrenzte Anzahl ungleicher Mittelwerte erhalten, die meisten komplizierter Natur.

Bei den Diffusionsversuchen schichtet man das Lösungsmittel vorsichtig über die Lösung. Man denkt sich eine normal zur Grenzschicht gelegte x-Achse. Der erhaltene Konzentrationsgradient y als Funktion von x stellt eine Kurve dar, die mehr oder weniger einer Gauss'schen Fehlerkurve gleicht. Berechnet man die Momente[1] (16) um das arithmetische Mittel, so erhält man mit Graléns Bezeichnungen u. a.

(Flächenmethode) $$D_{0,h} = \frac{1}{t} \cdot \frac{m_0^2}{4\pi H^2} \tag{9}$$

H = Höhe der Kurve.

(Momentmethode im engeren Sinne) $$D_{2,0} = \frac{1}{t} \cdot \frac{m_2}{2 m_0} \tag{10}$$

$$D_{4,2} = \frac{1}{t} \cdot \frac{m_4}{6 m_2}. \tag{11}$$

Auf polymolekulare Systeme angewendet geben diese Formeln die Mittelwerte

$$D_{0,h} = \left[\frac{\int_0^{c_0} dc}{\int_0^{c_0} \frac{dc}{\sqrt{D}}} \right]^2 \tag{12}$$

[1] $m_i = \int_{-\infty}^{+\infty} |x|^i \cdot y \cdot dx.$

$$D_{2,0} = \frac{\int_0^{c_0} D\, d\, c}{\int_0^{c_0} d\, c} = D_w \tag{13}$$

$$D_{4,2} = \frac{\int_0^{c_0} D^2\, d\, c}{\int_0^{c_0} D\, d\, c} = D_z \tag{14}$$

Man kann aus den Diffusionsversuchen D_w und D_z berechnen, dagegen nicht D_n.

Lamm und Gralén haben doch gezeigt, dass

$$D_{0,h} < D_w \tag{15}$$

und man kann auch zeigen, dass

$$D_{0,h} > D_n . \tag{16}$$

Definitionsgemäss erhält man nämlich

$$\frac{D_{0,h}}{D_n} = \frac{\int_0^{c_0} d\, c \cdot \int_0^{c_0} \frac{d\, c}{D}}{\left(\int_0^{c_0} \frac{d\, c}{\sqrt{D}}\right)^2} > 1 \,[1] \tag{17}$$

Daraus geht hervor, dass man trotz der Unmöglichkeit D_n zu berechnen, doch mit der Flächenmethode eine Diffusionskonstante erhalten kann, deren Wert zwischen D_n und D_w liegt.

Die Berechnung von D_w hat den grossen Vorteil gegenüber den anderen Formeln, dass sie Gewichtsmittel auch für schiefe Kurven liefert wo die Diffusionskonstante eine Funktion der Konzentration ist.

[1] Als ein Spezialfall der Schwartz'schen Ungleichheit ((15) Seite 38) gilt

$$\left(\int_a^b y\, d\, x\right)^2 < \int_a^b y^2\, d\, x \cdot \int_a^b d\, x .$$

Zur Anwendung von D_z ist zu bemerken, dass hierfür die Berechnung des 4. Moments der Diffusionskurve notwendig ist, was eine sehr grosse Genauigkeit des Experiments erfordert.

Sedimentation.

Auch bei den Messungen der Sedimentationsgeschwindigkeit verwendet man die Lamm'sche Skalenmethode. Durch Aufzeichnen der Skalenstrichverschiebungen (die dem Konzentrationsgradienten proportional sind) gegen den Abstand x von der Rotationsachse erhält man einen „Gipfel", in der Folge Sedimentationsbild genannt. Die Lage des Gipfels im Zeitpunkt t nach dem Beginn der Sedimentation sei x_t, die Lage des Meniskus x_0, die Winkelgeschwindigkeit $= \omega$.

Die Sedimentationskonstante wird folgendermassen definiert

$$s = \frac{dx}{dt} \cdot \frac{1}{\omega^2 x} \cdot \tag{18}$$

In der Lösung einer polymolekularen Substanz sedimentieren verschiedene Molekülgrössen ungleich rasch. Der Abstand $x_t - x_0$ ist für jede Molekülgrösse in erster Näherung der Sedimentationskonstante proportional, und das Sedimentationsbild ist deshalb nichts anderes als eine Verteilungskurve für s, wenn man

1. die Diffusion
2. die Konzentrationsabhängigkeit der Sedimentationskonstante
3. die Verdünnung auf Grund der Sektorform der Zentrifugenzelle ((5) Seite 7)
4. die Inhomogenität des Zentrifugalfeldes versäumt.

Von der Diffusion kann man nach Gralén absehen, wenn man es mit langen Fadenmolekülen zu tun hat. Für die Verdünnung auf Grund der Sektorform und die Inhomogenität des Zentrifugalfeldes können Korrektionen eingeführt werden, wenn notwendig, was aber im allgemeinen nicht der Fall sein dürfte. Dagegen kann die Konzentrationsabhängigkeit der Sedimentationskonstante nicht vernachlässigt werden. Ihr Einwirken auf das Sedimentationsbild wurde von Gralén näher untersucht ((14), Seite 13 u. ff.). Bei hinreichend grosser Ver-

dünnung müssen die Moleküle unabhängig voneinander sedimentieren und die Sedimentationskonstante wird praktisch konzentrationsunabhängig.

Die Ultrazentrifugierungen geben daher prinzipiell die Möglichkeit einer Bestimmung von s_n, s_w und s_z (und auch komplizierterer Mittelwerte) durch Extrapolation der aus den Sedimentationsbildern bei endlicher Konzentration erhaltenen Werte gegen die Konzentration Null hin.

Es wird sich weiter unten als bequem erweisen, eine Verteilungskurve für s zur Hand zu haben, und als solche verwenden wir wie Gralén (14) eine logarithmische Funktion

$$\begin{cases} \dfrac{d\,c}{d\,s} = K_s \cdot e^{-y^2} \\ \\ y = \dfrac{1}{\gamma_s} \cdot \ln \dfrac{s}{s_t} \end{cases} \tag{19}$$

wo K_s und γ_s Parameter sind und s_t die Abszisse für das Maximum der Verteilungskurve bedeutet.

Molekulargewichte aus Sedimentation und Diffusion.

Man erhält die Molekulargewichte durch Einsetzen der Werte für s und D in Svedbergs Formel (5). Es wird angenommen, dass die Sedimentationskonstante als s_n, s_w oder s_z, die Diffusionskonstante als D_n, D_w oder D_z bestimmt seien.

Es können neun verschiedene Molekulargewichte $M_{i,j}$ erhalten werden. Da für s_{index} und D_{index} zu (4) analoge Beziehungen bestehen, erhellt, dass $M_{z,n}$ am grössten und $M_{n,z}$ am kleinsten sein muss. Von besonderem Interesse ist $M_{w,w}$, da s_w und D_w am leichtesten experimentell zu bestimmen sind. Die nächste Aufgabe ist der Vergleich der Molekulargewichte $M_{i,j}$ mit den durch (1)—(3) definierten Molekulargewichten M_i. Durch Anwenden der Definitionen für die Mittelwerte von s und D findet man, dass das Verhältnis $M_{i,j}/M_i$ in keinem Fall konstant wird. Es geht daraus hervor, dass die aus Sedimentation und Diffusion bestimmten Molekulargewichte nicht in einfacher Beziehung zu den „Grundmittelwerten" M_n, M_w und M_z stehen.

$D = f(s)$ und die Verteilungsfunktion $dc/ds = F(s)$ werden als bekannt angenommen. Da erhält man

$$M_{w,w} = \frac{RT}{1 - V \cdot \varrho} \cdot \frac{\int_0^\infty s \cdot \frac{dc}{ds} ds}{\int_0^\infty f(s) \cdot \frac{dc}{ds} ds} \quad (20)$$

$$M_w = \frac{RT}{1 - V \cdot \varrho} \cdot \frac{\int_0^\infty \frac{s}{f(s)} \cdot \frac{dc}{ds} ds}{\int_0^\infty \frac{dc}{ds} ds} \cdot \quad (21)$$

Ähnliche Ausdrücke für andere M_i und $M_{i,j}$ sind leicht zu bilden.

Die Kenntnis von $D = f(s)$ zusammen mit Svedbergs Gleichung gibt die Möglichkeit, jede der Grössen M, s und D als Funktion von einer der anderen zu bestimmen. Mit dc/ds zusammen gibt dies die Möglichkeit die Verteilungsfunktionen dc/dM und dc/dD zu bestimmen.

Die exakte Lösung des Problems $M_{i,j}$ resp. $M_{i,j}/M_i$ zu bestimmen, erfordert folglich die Kenntnis einer Verteilungsfunktion und dazu eine Beziehung zwischen zwei der Quantitäten M, s und D.

Um weiter zu kommen, müssen wir explicite Ausdrücke für dc/ds und $f(s)$ suchen und wählen dazu für die erstere Gleichung (19) und für die letztere

$$D = f(s) = \frac{p}{s^{b-1}} \quad (22)$$

wo p und b Konstanten sind.

Letztere Gleichung geht aus einem Ansatz von Gralén ((14) Seite 102) hervor. Die Formel gilt theoretisch für sphärische Moleküle. Für diese gilt $b = 1{,}5$; für Fadenmoleküle ist b grösser. Tabelle 1 zeigt einige b-Werte aus der Literatur.

Tabelle 1. Die Werte von b in Gl. (22).

Substanz	b	Referenz
Polystyrol	1,56 [1]	SIGNER (17)
Nitrocellulose	6	GRALÉN (13)
Nitrocellulose	2,28 [1] 3,08 [1]	MOSIMANN (18)
Cellulose in Kupferoxydammoniak .	2,21	GRALÉN (14)
Cellulosexanthogenat	2,07	»
Nitrocellulose	3,17	»

[1] Berechnet vom Verfasser.

Setzt man (19) und (22) für dc/ds resp. $f(s)$ ein, so können sämtliche Integrale in (20), (21) und analogen Gleichungen auf das Integral

$$\begin{cases} I = \int_0^\infty s^\mu \cdot e^{-y^2}\, ds \\ y = \dfrac{1}{\gamma_s} \cdot \ln s/s_t;\ \mu \text{ eine beliebige Zahl} \end{cases} \tag{23}$$

zurückgeführt werden. Dessen explicite Form ist

$$I = \sqrt{\pi} \cdot \gamma_s \cdot s_t^{\mu+1} \cdot e^{\frac{\gamma_s^2(\mu+1)^2}{4}}. \tag{24}$$

Man setzt $s^\mu = s_t^\mu \cdot e^{\mu \cdot \ln s/s_t}$. Durch die Substitution $\ln s/s_t = v$ wird der Exponent von e

$$-\frac{1}{\gamma_s^2} v^2 + v(\mu + 1). \tag{25}$$

Man komplettiert das Quadrat im Ausdruck 2. Grades und kann dann durch Substitution das Integral auf das gewöhnliche Wahrscheinlichkeitsintegral zurückführen, womit die Lösung gegeben ist.

M_i und $M_{i,j}$ erhalten die Form

$$M_{\text{index}} = \frac{RT}{1 - V \cdot \varrho} \cdot \frac{s_t^b}{p} \cdot e^{\frac{\gamma_s^2 \psi'(b)}{4}} \tag{26}$$

Tabelle 2. Die Funktion ψ für verschiedene M_i und $M_{i,j}$.

M_{index}	ψ	M_{index}	ψ
M_n	$-b^2 + 2b$	$M_{n,w}$	$-b^2 + 4b - 2$
M_w	$b^2 + 2b$	$M_{w,w}$	$-b^2 + 4b$
M_z	$3b^2 + 2b$	$M_{z,w}$	$-b^2 + 4b + 2$
$M_{n,n}$	b^2	$M_{n,z}$	$-3b^2 + 8b - 4$
$M_{w,n}$	$b^2 + 2$	$M_{w,z}$	$-3b^2 + 8b - 2$
$M_{z,n}$	$b^2 + 4$	$M_{z,z}$	$-3b^2 + 8b$

wo ψ eine Funktion 2. Grades von b ist, mit Koeffizienten die einfache ganze Zahlen oder Null sind. Eine Zusammenstellung gibt Tabelle 2.

Die Quotienten $M_{i,j}/M_i$ erhalten die Form

$$M_{i,j}/M_i = e^{\frac{\gamma_s^2 \cdot \varphi(b)}{4}} \tag{27}$$

wo φ ebenfalls eine Funktion 2. Grades von b ist, deren Koeffizienten man leicht mit Hilfe von Tabelle 2 findet.

Numerische Berechnungen wurden für verschiedene Werte von b und γ_s ausgeführt. In den Diagrammen wurde $M_w = 100$ angenommen. Man kann folgende Schlüsse ziehen:

1. Molekulargewichte aus Sedimentation und Diffusion liegen im allgemeinen zwischen M_n und M_w.

2. Mit steigenden Werten von b sinkt der Wert von $M_{i,j}$.

3. Die verschiedenen $M_{i,j}$ können in Gruppen zusammengefasst werden. Für $b = 1{,}5$ bestimmt die Berechnungsmethode für s, welcher Gruppe $M_{i,j}$ zugehört, für $b = 3$ oder höher ist es im Gegensatz dazu D, welches die Gruppe bestimmt.

4. Sind für eine Substanz die Konstante b und ein $M_{i,j}$ bekannt und dazu *einer* der Werte M_n, M_w oder M_z, durch osmotische Messung oder Sedimentationsgleichgewicht erhalten, so ist hierdurch der Wert von γ_s festgelegt, vorausgesetzt dass der Ansatz für die Verteilungsfunktion richtig ist.

5. Sind für eine Substanz die Konstante b und ein $M_{i,j}$ bekannt und dazu *zwei* der Werte M_n, M_w oder M_z, so kann

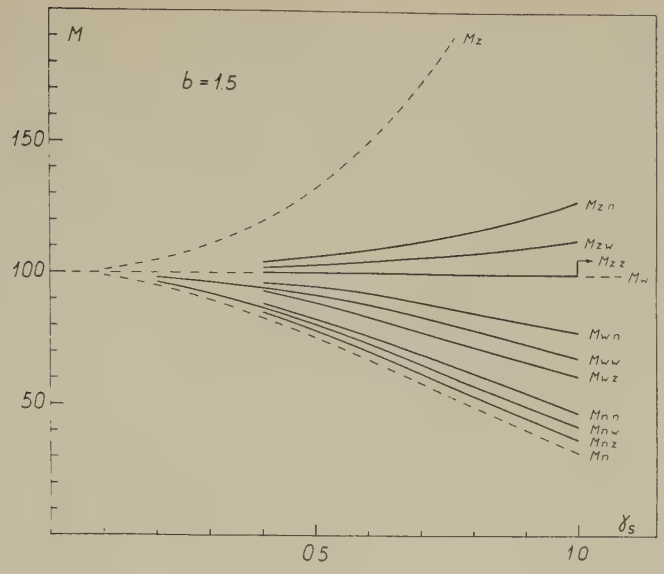

Fig. 1.

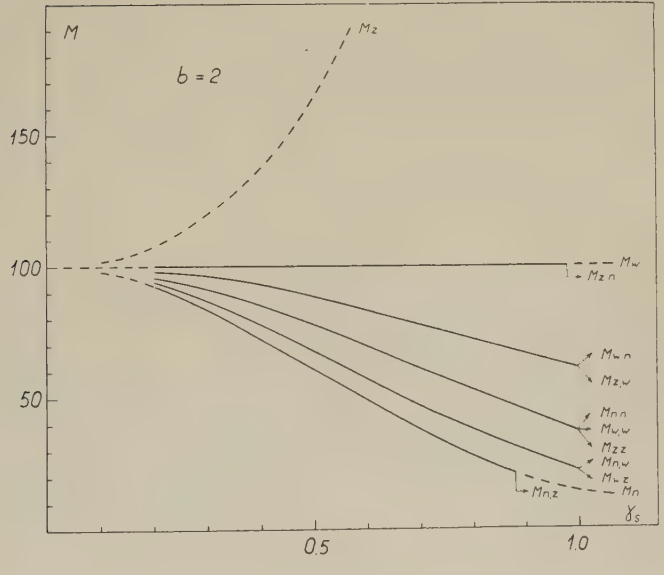

Fig. 2.

Fig. 1—2. Werte von M_i und $M_{i,j}$ als Funktion von γ_s für verschiedene b.

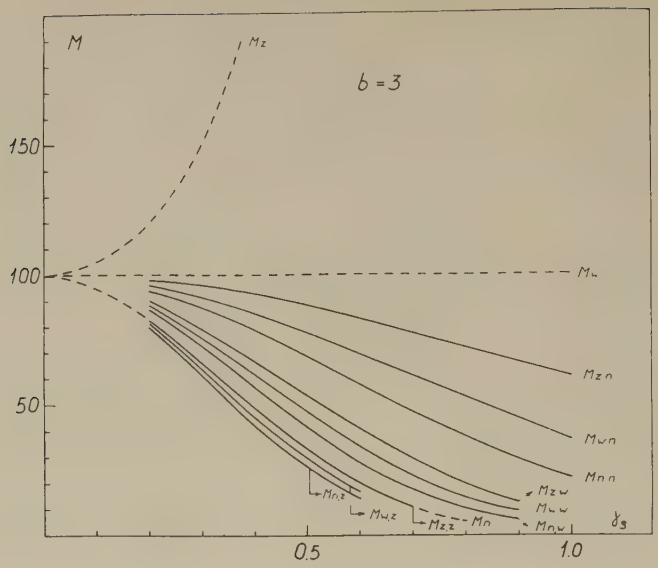

Fig. 3.

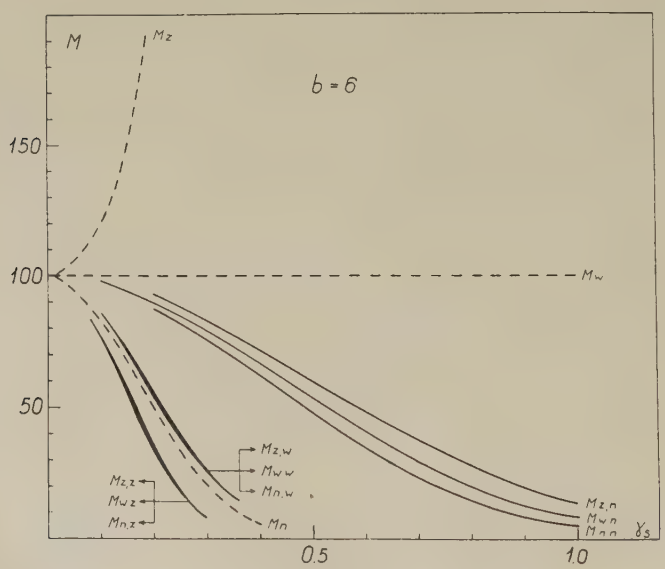

Fig. 4.

Fig. 3—4. Werte von M_i und $M_{i,j}$ als Funktion von γ_s für verschiedene b

man gleichzeitig prüfen, ob der Ansatz richtig ist und γ_s bestimmen.

Um die obigen Rechnungen durchzuführen, waren wir gezwungen eine besondere Form der Verteilungsfunktion dc/ds anzunehmen. Ein theoretischer Grund für diese Form existiert nicht. Eigene Untersuchungen (unpubliziert) an Nitrocellulosen haben doch mehrmals gezeigt, dass die Kurve dc/ds eine positive Schiefe hat ((16) Seite 162) und folglich mit (19) in einem wesentlichen Punkt übereinstimmt. Die Rechnungen sollen auch auf andere Typen von Verteilungsfunktionen ausgedehnt werden. Es ist doch nicht zu erwarten, dass dadurch etwas qualitativ Neues herauskommen wird.

Die Sedimentationskonstante polymolekularer Substanzen wurde bisher im allgemeinen aus der Geschwindigkeit bestimmt, mit der sich das Maximum des Gradienten verschiebt. Man erhält auf diese Weise die wahrscheinlichste Sedimentationskonstante s_t, welche keinen statistisch definierten Mittelwert darstellt. Aus theoretischen Gesichtspunkten ist es geeigneter s_n, s_w oder s_z zu bestimmen. Mit Hinsicht auf die experimentellen Schwierigkeiten ist s_w der Vortritt zu geben. Solange das Sedimentationsbild symmetrisch ist, fällt s_w, das arithmetische Mittel, mit s_t zusammen, und für mässige Schiefe der Sedimentationsbilder kann man die aus der Statistik entlehnte approximative Beziehung ((16) Seite 125) anwenden.

$$s_w = \frac{3\,s_m - s_t}{2} \tag{28}$$

wo s_m der Zentralwert ist.[1]

Da die Schiefe des Sedimentationsbildes nicht besonders ausgeprägt zu sein pflegt, kann man annehmen, dass bisher publizierte Molekulargewichte aus Sedimentation und Diffusion am ehesten $M_{w,w}$ entsprechen, vorausgesetzt, dass die Diffusionskonstante nach der Momentmethode berechnet war.

[1] Definiert durch die Beziehung

$$\int_0^{s_m} \frac{dc}{ds}\,ds = \int_{s_m}^{\infty} \frac{dc}{ds}\,ds.$$

Zusammenfassung.

Molekulargewichte können durch Svedbergs Formel, Gl. (5) bestimmt werden. Man nimmt an, die Sedimentations- und Diffusionskonstanten seien als Zahl-, Gewichts- oder *Z*-Mittelwerte berechnet. Bei Annahme einer logarithmischen Verteilungsfunktion (19) für die Sedimentationskonstanten und eine Beziehung zwischen Sedimentations- und Diffusionskonstanten von der Form von Gl. (22), sind für verschiedene Fälle Formeln hergeleitet und zahlenmässige Berechnungen für verschiedene Werte der eingehenden Parameter ausgeführt worden. Als Resultat erhielt man, dass Molekulargewichte aus Sedimentation und Diffusion im allgemeinen zwischen Zahl- und Gewichtsmittel liegen. Kennt man ein Molekulargewicht aus Sedimentation und Diffusion, und dazu noch einen oder mehrere der einfachen Molekulargewichtsmittelwerte so können Schlüsse auf die Verteilungsfunktion der Moleküle gezogen werden. Die geeignetste Methode der Bestimmung von Sedimentationskonstanten wird diskutiert.

Diese Arbeit geht als ein Teil in eine allgemeine Untersuchung über Nitrocellulose ein, die am physikalisch-chemischen Institut in Uppsala im Auftrag und in Zusammenarbeit mit A. B. Bofors, Abt. Nobelkrut, Nitroglycerinaktiebolaget und A. B. Expressdynamit betrieben wird. Es ist mir eine angenehme Pflicht den Direktoren dieser Unternehmen für die auf diese Weise erhaltene Unterstützung zu danken.

Der Verfasser wünscht Dozent Nils Gralén für gute Ratschläge und wertvolle Diskussionen zu danken.

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The Theory of Sedimentation Equilibrium and the Determination of a Thermodynamic Factor Occurring in the General Diffusion Equation.

By Ole Lamm.

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It has long been recognized that the sedimentation equilibrium in a gravitational or centrifugal field is capable of giving information regarding the thermodynamic properties of pure substances or solutions. The possibilities of the ultracentrifuge in this direction have often been theoretically considered and experimentally utilized.[1] It is the object of this paper to present the general condition for the sedimentation equilibrium in a form suitable for the determination of a thermodynamic factor, which plays an importante rôle especially in the interpretation of diffusion coefficients for non-ideal solutions. This factor can often be ascertained from partial pressure data, a procedure practicable for sufficiently volatile solutions, especially if the vapour mixture is ideal. Such calculations from available vapour pressure data were made by Eyring and collaborators (1), unfortunately without recording their results, which can only be derived from diagrams. It was pointed out by Lemonde (2) that the vapour pressure data for binary mixtures do not refer to the temperature at which the diffusion coefficient may most conveniently be (and actually has been) measured. The present state of experimental knowledge in this field is evidently unsatisfactory.

[1] For comprehensive treatises and literature see Svedberg and Pedersen, "The Ultracentrifuge", Oxford 1940; Lewis and Randall, "Thermodynamics", New York 1923; Andrews in "A Commentary on the Scientific Writings of J. W. Gibbs", New Haven 1936.

The Thermodynamic Factor.

The general equation for the diffusion of a two component system is (cf. (3) and (4))[1]

$$\frac{\partial n}{\partial t} = RT\frac{\partial}{\partial x}\left(\frac{B_{12}}{\Phi_1 + \Phi_2}\frac{\partial n}{\partial x}\right). \tag{1}$$

The diffusion coefficient should be written

$$D_{12} = \frac{RTB_{12}}{\Phi_1 + \Phi_2}, \tag{2}$$

which is symmetrical with respect to the two components, the diffusion being an altogether reciprocal process. The equations only take into consideration the one-dimensional diffusion, free of convections, including the condition that no volume change accompany the mixing process. The thermodynamic factor is

$$B_{12} = 1 + \frac{\partial \ln f_1}{\partial \ln N_1} = 1 + \frac{\partial \ln f_2}{\partial \ln N_2}, \tag{3}$$

N and f being the mole fractions and the corresponding activity coefficients. The proof of equation (1) is most simply performed by adapting the calculations made in (4) for the three-component system to the simpler case of two components. The factor (3) has been obtained before by several investigators as a generalization of Fick's law by substituting the chemical potential gradient for the concentration gradient, see e. g. Schreiner (5). Onsager and Fuoss (6), Dehlinger (7), van Rysselberghe (8). It should be possible to determine the factor B_{12} from the sedimentation equilibrium, as we shall now proceed to show theoretically.

Symbols Employed in the Calculations.

M molecular weight.
N mole fraction, f corresponding activity coefficient.
V partial specific volume.

[1] n is the concentration of one of the components in mol/lit., t the diffusion time, x the diffusion direction, Φ_1 and Φ_2 the mutual frictions in volumes which contain one mole of component 1 and component 2 respectively B_{12} is the thermodynamic factor in question.

n_{12} refractive index.
ω angular velocity.
x distance from axis of rotation.
ϱ density of solution.
B_{12} thermodynamic factor.

Theory of Sedimentation Equilibrium.

The general equilibrium condition for a component of a solution in a centrifugal field, deduced by PEDERSEN (9) from the original statement of GIBBS, provides a suitable point of departure for our calculation. The condition is, for the two independent components,

$$R\,T\,d\,\ln\,N_1 f_1 = M_1(1 - V_1\,\varrho_x)\,\omega^2\,x\,dx \tag{4}$$

$$R\,T\,d\,\ln\,N_2 f_2 = M_2(1 - V_2\,\varrho_x)\,\omega^2\,x\,dx \tag{5}$$

where ϱ_x, the variable density of the solution, is

$$\varrho_x = \frac{M_1 N_1 + M_2 N_2}{M_1 N_1 V_1 + M_2 N_2 V_2}\,; \tag{6}$$

the ratio of the mean "molecular weight" and the "molar volume" of the mixture. Now,

$$d\,\ln\,N_2 f_2 = \frac{1}{N_2}\left(1 + \frac{\partial\,\ln f_2}{\partial\,\ln N_2}\right) d\,N_2 = B_{12}\,d\,\ln\,N_2,$$

so that the condition (5) for component 2 may also be formulated

$$R\,T\,B_{12}\,d\,\ln\,N_2 = M_2(1 - V_2\,\varrho_x)\,\omega^2\,x\,dx.^1 \tag{7}$$

For practical purposes, in the case of molecular weight determinations on high molecular compounds, it is usual to put $B_{12} = 1$, to integrate this equation (7) assuming ϱ_x constant, and to replace N_2 by the concentration, all these approximations being correct when the concentration tends to zero. The problem is thus treated unsymmetrically (with component 2 as solute), and the equilibrium condition for the solvent is left out of consideration. In the case of the binary mixture in

[1] Eliminating ϱ_x between this equation and the corresponding expression for component 1, equation (9) is obtained.

general, it would be of interest to bring the equilibrium condition into a more symmetrical form. Combining equations (6) and (7):

$$R\,T\,B_{12}\,d\,N_2 = \frac{M_1\,M_2\,N_1\,N_2\,(V_2 - V_1)}{M_1\,N_1\,V_1 + M_2\,N_2\,V_2}\,\omega^2\,x\,dx. \qquad (8)$$

On reducing the right-hand member by $M_1\,M_2\,N_1\,N_2\,V_1\,V_2$ and taking $d\,N_2 = -\,d\,N_1$, this may be written

$$\frac{1}{M_2\,V_2}\,d\,\ln\,N_2 - \frac{1}{M_1\,V_1}\,d\,\ln\,N_1 = \left(\frac{1}{V_2} - \frac{1}{V_1}\right)\frac{\omega^2}{R\,T\,B_{12}}\,x\,dx. \qquad (9)$$

If the sedimentation is not too pronounced, the separation of components will be small, and it should be possible to integrate equation (9) assuming the thermodynamic factor B_{12} and (if it is allowable to neglect the compressibility effect) the partial specific volumes V_1 and V_2 to be constant. Integration between two points x' and x'' in the cell gives the symmetrical relation

$$\ln\left[\left(\frac{N_2''}{N_2'}\right)^{\frac{1}{M_2\,V_2}}\left(\frac{N_1'}{N_1''}\right)^{\frac{1}{M_1\,V_1}}\right] = \left(\frac{1}{V_2} - \frac{1}{V_1}\right)\frac{\omega^2\,(x''^2 - x'^2)}{2\,R\,T\,B_{12}}, \qquad (10)$$

where $M_1\,V_1$ and $M_2\,V_2$ are the partial molar volumes of the components. These, the factor B_{12} and especially the difference of the inverted partial specific volumes determine the degree of sedimentation in the centrifugal field in question.

Incidentally, it is of interest to write down the expression which is obtained from equation (10) for a dilute solution of component 2 in component 1. In this case N_1 is very nearly constant throughout the liquid column, and we may put $N_1'/N_1'' = 1$.[1] Thus

$$M_2 = \frac{2\,R\,T\,B_{12}\,\ln\,\dfrac{N_2''}{N_2'}}{\left(1 - \dfrac{V_2}{V_1}\right)\omega^2\,(x''^2 - x'^2)}. \qquad (11)$$

It should be remembered that on integrating equation (9)

[1] If component 2 is a high molecular substance and $M_1 \ll M_2$; the exponent of N_1'/N_1'' in equation (10) is comparatively great. This will increase the error of the approximation.

B_{12} was assumed to be constant, which will often be too rough an approximation, especially if component 2 is an electrolyte (cf. PEDERSEN (9) and DRUCKER (10)). The factor $(1 - V_2/V_1)$ is, however, of interest. The simple integration of equation (5) leads to the common, analogous expression with the factor $(1 - V_2 \varrho_x)$. It has been discussed wether ϱ is the density of the solution or that of the solvent. In equation (5) ϱ_x certainly means the density of the solution. However, if on performing the integration this quantity is considered as a function of x, equation (11) results. Thus, it seems that in the factor $(1 - V\varrho)$, ϱ may also be interpreted as the inverted partial specific volume of the solvent. It does not seem possible to make a general statement regarding the most adequate approximation, this being dependent on the numerical conditions. — According to equation (6) ϱ_x and $1/V_1$ are, of course, identical at infinite dilution. — Equation (10) may, however, be used for obtaining a more exact integrated expression for M_2 than represented by equation (11) or by the usual interpretation with ϱ_x. We have

$$\ln \frac{N_1''}{N_1'} = \ln \frac{1 - N_2''}{1 - N_2'} \approx N_2' - N_2''$$

and obtain, by comparison with (11), a correction term Q according to

$$M_2 = \frac{2\,R\,T\,B_{12} \ln \dfrac{N_2''}{N_2'}}{(1 - V_2/V_1)\,\omega^2 (x''^2 - x'^2) - Q}; \qquad (12)$$

$$Q = \frac{2\,R\,T\,B_{12}\,V_2 (N_2'' - N_2')}{M_1\,V_1}. \qquad (13)$$

The correction may amount to a few per cent in M_2.

The Determination of B_{12}.

For the experimental determination of B_{12} in the ultracentrifuge it ought not to be necessary to integrate equation (8). If a refractometric method is used in measuring the gradient of the mole fractions (n_{12} = refractive index), we have

$$\frac{d N_2}{d x} = \frac{d n_{12}}{d x} \Big/ \frac{d n_{12}}{d N_2}. \tag{14}$$

Hence (8) becomes

$$B_{12} = \frac{M_1 M_2 N_1 N_2 (V_1 - V_2)}{M_1 N_1 V_1 + M_2 N_2 V_2} \frac{\omega^2}{R T} \frac{\frac{d n_{12}}{d N_2}}{\frac{1}{x} \frac{d n_{12}}{d x}}. \tag{15}$$

There is reason to believe that, in not too strong a centrifugal field, $\frac{1}{x} \frac{d n_{12}}{d x}$ will be constant throughout the centrifuge cell. $\frac{d n_{12}}{d N_2}$ should be determined by differential measurements of refractive index; moreover it is, eventually, transformed to another concentration unit. Assuming the Dale—Gladstone relation for refractivity, numerical calculations have shown that the refractive index gradient is of measurable magnitude for most mixtures in centrifugal fields which are conveniently attained in the "equilibrium" centrifuge of Svedberg, e. g. mixtures of organic liquids the material constants of which are not too nearly equal. On the other hand, a probable sensitivity of the method to impurities must be considered, the use of uncemented cells being desirable.

A matter of practical importance is the time t_m seconds necessary for the attainment of equilibrium in the case of ordinary binary mixtures. According to a formula deduced by Pedersen (11),

$$t_m = \frac{2 (x_n - x_0)^2}{D \ln \frac{c_n}{c_0}},$$

this time should be short because of the high diffusion constant D, but long if the concentration (c_n) at the bottom of the centrifuge cell is very nearly equal to that at the meniscus (c_0). The height of the column, $x_n - x_0$, will have to be small. The adjustment is probably more rapid than would appear from the formula quoted, the relative concentration changes being particularly small in work with concentrated solutions.

Conclusions.

Attention has been directed to the possibility of an ultracentrifugal determination of the thermodynamic factor

$$\left(1 + \frac{\partial \ln f}{\partial \ln N}\right),$$

for binary solutions in general, through the sedimentation equilibrium. In deducing the equations required, some observations regarding the usual interpretation of the sedimentation equilibrium have been made, which should be considered in certain cases of precision molecular weight determination by the method in question.

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Experiments in Calculating the Actual Mineralogical Composition of Ceramic Silica Bricks by the Aid of Differential Thermal Analysis.

By R. Norin.

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In 1939 Norton (1) published a paper entitled "Critical study of the differential thermal method for the identification of the clay minerals". Norton here emphasized the great differences in the heat absorption curves for the clay minerals as computed by the differential thermal method. This method provides us with the possibility of determining relatively the heat quantities, which are absorbed or given off during a chemical reaction or at the transition point of a mineral modification. Regarding the experimental technique the present author refers to the paper by Norton cited above and to an earlier paper of his own in Geologiska Föreningens Förhandlingar for 1941 (2).

Several authors have criticized the method in respect of the reproducibility of values. By special arrangements concerning, in the first place, the electrical heating control we have achieved a high degree of constancy in the power consumption. This has encouraged us to attack the more involved problem of quantitative determinations. In the beginning we confined our efforts to the dehydration effect of kaolinite, analyzing different quantities in exactly the same way. After the plotting of the curves the areas of the surfaces between them and the temperature axis were determined planimetrically. We could then establish the constancy of the ratios of the curve areas and the kaolin quantities. In the present case, where the quantities treated represented the ratios 1.5, 1.0 and 0.5, the area ratios were identical with these. Thus, with a definite concentration of the reference kaolinite, we are able

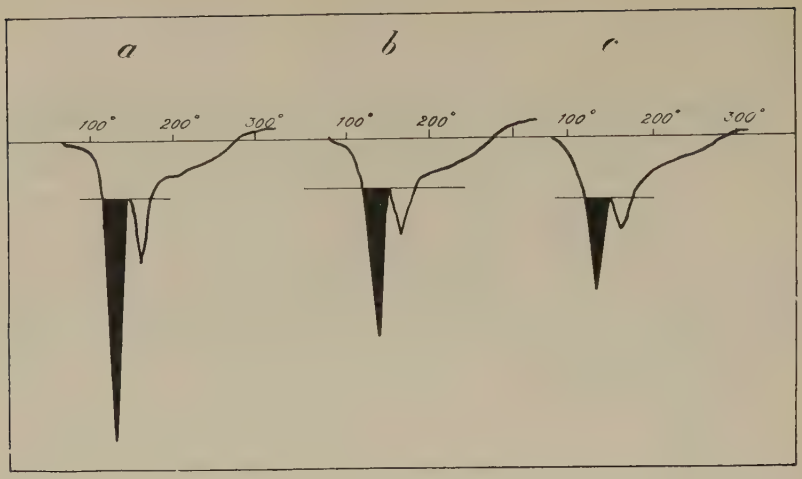

Fig. 1.

to make quite satisfactory quantitative estimations of the clay kaolinite.

In the early thirties our company was engaged in intensive efforts to find a dilatometrical method for the determination of the different silica minerals. According to the trial method test rods were made of pulverized silica and some clay. The dried rods were placed in a dilatometer and the dilatation-temperature curves were subjected to mathematical analysis. Unfortunately there proved to be fundamental discrepancies between the results obtained and some controllable facts concerning the relative concentrations of the silica minerals. Anyhow, as the experiments with kaolinite had given good results, the author attacked the silica problems on the basis of the differential method. The silica modifications actually differ very considerably with respect both to their transformation temperatures and to the quantities of their transformation energy.

As starting point we took a very well tridymitized silica which was first subjected to minute microscopical examination. On the microscopical slides we could establish the absence of free quartz. The results of the thermal analysis are shown in Fig. 1. Here we find the transition points of tridymite very well marked at the temperatures between 100° and 200°.

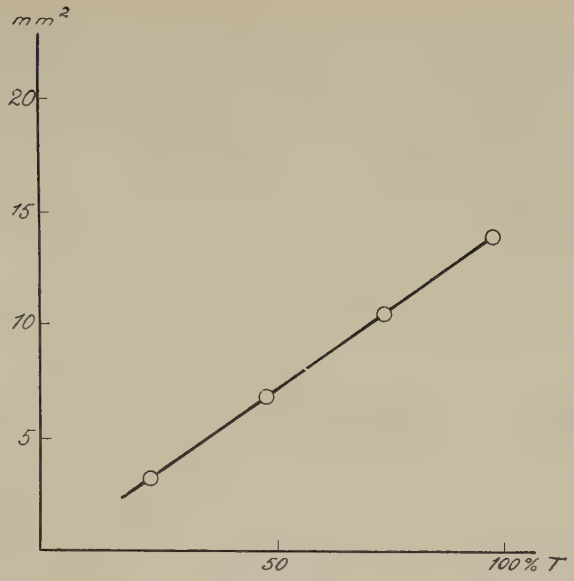

Fig. 2.

No cristobalite effect whatever is to be observed. Nor is any effect associated with the β—α-quartz transition point obtained.

The diagrams in Fig. 1 refer to three different experiments. No. 1 concerns a 100 per cent tridymite material. No. 2 a 50 per cent tridymite material with 50 per cent pure quartz and No. 3 a 25 per cent tridymite material with 75 per cent pure quartz. The equivalent curve areas of diagrams a—c were measured with the planimeter, and the values were plotted in the diagram shown in Fig. 2, where the abscissa indicate the tridymite quantities in the specimens. The 75 : 25 ratio of the mixture tridymite-pure quartz was also analyzed. The results here also corresponded very well with the diagram in fig. 2.

Thus, in the case of the tridymite we also obtained a very nice proportionality between the curve areas and the quantities treated.

With regard to the cristobalite, it is impossible to fix its amount quantitatively under the microscope. The tridymite also presents difficulties, partly because of the minuteness of the crystals, partly because the silica often shows transitional

stages between tridymite and amorphous SiO_2. On the other hand, the free quartz is, in most cases, rather simple to determine by the aid of the microscope integration table. The silicates in the silica might be estimated fairly accurately by chemical analysis.

After summing up the possibilities of calculating the actual composition of silica bricks we arrive at the following procedure:

1. Estimation of silicates by chemical analysis.
2. Calculation of free quartz by the aid of the integration table.
3. Estimation of tridymite by the differential thermal analysis technique just described.
4. Estimation of cristobalite by difference from 100 per cent.

By the above remarks the author would call attention to the possibilities offered by the refined method of differential thermal analysis. Special regard should be paid to the possible applications of quantitative thermal analysis to such ceramic minerals as show thermal effects on heating or cooling.

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A Method for the Determination of Diffusion Constants.

By Olof Quensel.

The following method for the determination of diffusion constants was worked out at the Institute of Physical Chemistry in Upsala when the author was a pupil of Professor The Svedberg. As the author's work became directed towards other problems, only a few tentative experiments were made. The general principles may, however, be of a certain interest.

In the present paper a short review will be given of the theory of the method. The experimental procedure and some diffusion measurements on phycoerythrin will be dealt with in brief. The method is applicable only under the condition that the solution of the substance, whose diffusion constant is to be determined, has a light absorption different from that of the solvent.

Theory.

In a vertical diffusion cell a layer of the solution to be investigated is formed under the pure solvent. A parallel, homogeneous beam of light falls upon the cell perpendicular to the direction of diffusion. This beam is limited by a rectangular slit, the upper and lower edges of which are at such a great distance from the original boundary that no appreciable concentration changes are observed there during the period when the diffusion is followed.

If the light absorption of the solution differs from that of the solvent, the luminous flux through the diffusion cell will fall off with time. This can be seen from the following reasoning.

In two horizontal differential layers of solution at distances $+x$ and $-x$ from the original boundary, the concentration

changes per unit time $\frac{dc}{dt}$ are, according to the laws of diffusion, numerically equal. For positive values of x (x being counted positive in the direction of diffusion) $\frac{dc}{dt}$ is, however, positive, and for negative values of x negative. Since the concentration at the distance $+x$ is less than that at $-x$, it follows from Beer's law that the decrease in intensity per unit time for the light which has passed through the layer at a distance $+x$ is greater than the corresponding increase in intensity at the distance $-x$. The total luminous flux through these two layers will thus decrease with time. As the whole diffusion zone may be divided into such pairs of layers, it immediately follows that the total luminous flux through the diffusion zone will also decrease with time.

On this basis the following method for determining diffusion constants has been worked out.

Let, at a certain time, $d\Phi$ be the luminous flux through a horizontal layer of height dx at a distance x from the original boundary. Then we may write

$$d\Phi = \frac{\Phi_c}{a} dx \qquad (1)$$

where Φ_c is the luminous flux which would pass through the cell if the concentration therein was constant throughout and equal to the concentration in the layer under consideration. a is the distance between the upper and lower edges of the slit, i. e. the extension of the beam in height.

For the total luminous flux through the diffusion cell we have, according to (1)

$$\Phi = \frac{1}{a}\int_{x_1}^{x_2} \Phi_c\, dx = \frac{1}{a}\left(\Phi_{c_2} x_2 - \Phi_{c_1} x_1 - \int_{\Phi_{c_1}}^{\Phi_{c_2}} x\, d\Phi_c\right) \qquad (2)$$

where x_1 and x_2 are the distances from the original boundary to the lower and upper edges of the slit respectively. Φ_{c_1} and Φ_{c_2} are the luminous fluxes which would pass through the cell if it were filled with the original solution and the pure solvent respectively.

If we let Φ_0 indicate the luminous flux through the cell at the commencement of the diffusion (time $t = 0$), i. e. when there is a sharp boundary between the solution and the solvent, then

$$\Phi_0 = \frac{1}{a}(\Phi_{c_2} x_2 - \Phi_{c_1} x_1)$$

whence, according to (2)

$$\Phi = \Phi_0 - \frac{1}{a}\int_{\Phi_{c_1}}^{\Phi_{c_2}} x \, d\, \Phi_c \tag{3}$$

The concentration distribution in the diffusion cell is at any instant determined by the well-known equation

$$c = \frac{c_0}{2}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{D\,t}}} e^{-u^2}\, d\, u\right) \tag{4}$$

where c is the concentration of the solution at a distance x from the original boundary, c_0 is the original concentration of the solution and D is the diffusion constant. It follows from (4) that $\frac{x}{2\sqrt{D\,t}}$ is a function of the concentration. We may therefore write

$$\frac{x}{2\sqrt{D\,t}} = f(c).$$

Equation (3) may now be written

$$\Phi = \Phi_0 - \frac{2\sqrt{D\,t}}{a}\int_{\Phi_{c_1}}^{\Phi_{c_2}} f(c)\, d\, \Phi_c \tag{5}$$

whence it follows that Φ must be a linear function of $\sqrt{t}$.

From (5) we have

$$\frac{\partial \Phi}{\partial \sqrt{t}} = -\frac{2\sqrt{D}}{a}\int_{\Phi_{c_1}}^{\Phi_{c_2}} f(c)\, d\, \Phi_c. \tag{6}$$

If the value of $\Phi_0 - \Phi$ for $t = \frac{1}{D}$ be written as A, we obtain according to (5)

$$A = \frac{2}{a} \int_{\Phi_{c_1}}^{\Phi_{c_2}} f(c)\, d\, \Phi_c. \tag{7}$$

Finally, if $\frac{\partial \Phi}{\partial \sqrt{t}}$ be put equal to k, we have, according to (6) and (7),

$$D = \left(\frac{k}{A}\right)^2. \tag{8}$$

By a suitable experimental arrangement Φ can be determined at different times. Then k can also be obtained, since it is the slope of the straight line giving the relationship between $\sqrt{t}$ and Φ.

To obtain A, i. e. the theoretical decrease in the luminous flux after a time $\frac{1}{D}$, the diffusion cell is filled with the solution under investigation in different concentrations and the corresponding values of the luminous flux Φ_c are determined experimentally. If the corresponding values of $\frac{c}{c_0}$ and $\frac{\Phi_c}{a}$ are plotted on a graph a curve is obtained of the type shown in Fig. 1. According to (4) (the integral is tabulated) the values of $\frac{c}{c_0}$ and x are determined for $D\bar{t} = 1$. (The broken curve in

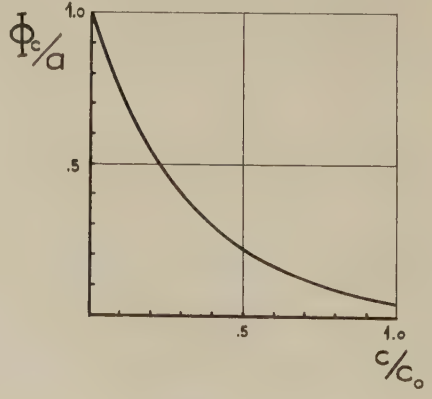

Fig. 1.

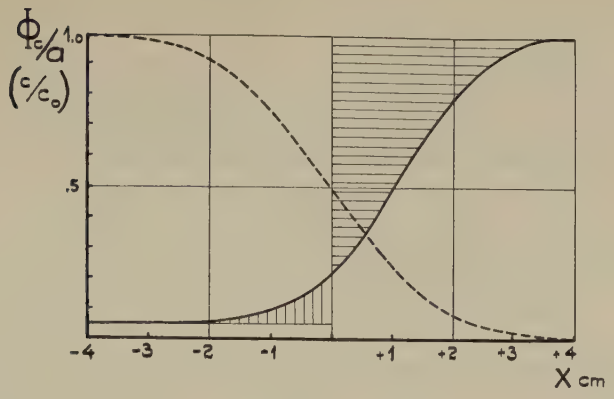

Fig. 2.

Fig. 2.) Now $\frac{\Phi_c}{a}$ can easily be plotted as a function of x, valid for $Dt = 1$. A curve is obtained similar to the full drawn curve in Fig. 2. A is afterwards obtained as the difference between the horizontally shaded and vertically shaded areas.

The measurement of lengths, necessary in all diffusion determinations, is limited in the present procedure to a measurement of the distance a between the lower and upper edges of the slit. This distance need, however, only be known in the experiments where the relation between $\frac{c}{c_0}$ and $\frac{\Phi_c}{a}$ is determined. In the diffusion experiments themselves, a need not be known, since for different values of a the straight line giving the relationship between $\sqrt{t}$ and Φ will only undergo parallel displacements in the direction of height. This is unimportant, since for the calculation of D only the slope of this line need be known.

Experimental Procedure.

In these preliminary experiments the apparatus was relatively primitive, consisting partly of components which are now obsolete. Its detailed description is therefore devoid of real interest. The principal features will, however, be given.

A condensor system provided a homogeneous, parallel beam. After passing through the slit and the diffusion cell this fell upon

a photoelectric measuring device to which a mirror galvanometer was coupled.

The measurements were made as follows. The parallel beam was first passed through the diffusion cell, and the galvanometer deflection corresponding to the luminous flux through the cell was measured. The beam was then so deflected that it passed instead through a measuring arrangement consisting of a system of polarising prisms. By rotating one of these prisms the luminous flux through the measuring arrangement could be so regulated that the galvanometer deflection was the same as that obtained when the light had passed through the diffusion cell. After a reading of the angle of rotation of the movable prism, the luminous flux through the diffusion cell could be determined in arbitrary units.

Determination of the Diffusion Constant of Phycoerythrin.

As an illustration of the applicability of the method a short account is given of a determination of the diffusion constant for phycoerythrin. Four different experiments were carried out with one and the same initial solution. The results of these experiments are shown graphically in Fig. 3. The unit for the time t was the second; that for the luminous flux Φ through the diffusion cell was arbitrary. The figure shows that the experimentally determined relationship between $\sqrt{t}$ and Φ is linear, in agreement with the theory. The parallel displacements of the straight lines in the height direction arise from the fact that the original boundary in the different experiments lay at different heights in relation to the rectangular slit in front of the diffusion cell.

The slopes k of the straight lines in Fig. 3 are given in the table below. Since the same initial solution was used in all experiments, A, the theoretical decrease in the luminous flux through the diffusion cell after a time $\frac{1}{D}$, had the same value in all cases. A is calculated in the manner described in the theoretical section.

From the values of k and A thus obtained the diffusion constant D was calculated from (8). The unit was cm^2/sec.

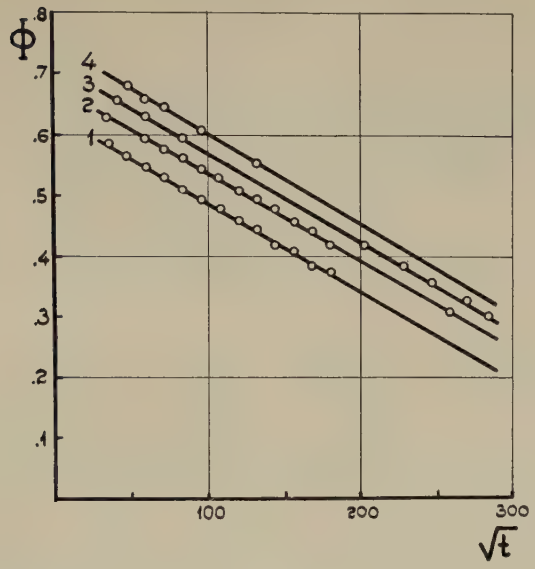

Fig. 3.

Experiment no.	k	A	$D \times 10^7$ cm²/sec.
1	−0.00146	2.28	4.10
2	−0.00143	2.28	3.93
3	−0.00145	2.28	4.04
4	−0.00148	2.28	4.21
Mean: $D = 4.07 \times 10^{-7}$			

Accurate determinations of the diffusion constant of phycoerythrin carried out according to another method (1) have given the value 4.00×10^{-7} cm²/sec.

References.

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Beitrag zur Kenntnis der Theorie des elektrooptischen Effektes in Kolloiden.

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In den letzten Jahren sind Messungen der elektrooptischen Doppelbrechung an in Wasser gelösten Kolloiden ausgeführt worden, eine Theorie der hierbei auftretenden Effekte liegt jedoch noch nicht vor.

Da man nur ausnahmsweise mit einem dispersen System am isoelektrischen Punkte zu tun hat, ist zwecks Vermeidung von durch Kataphorese verursachten Konzentrationsänderungen für das Studium der Doppelbrechung das elektrische Wechselfeld angewendet worden. Wir wollen deshalb im folgenden einige Fälle von Doppelbrechung im Wechselfeld unter dem Gesichtspunkte der Orientierungstheorie untersuchen.

Eine Partikel kann durch gewisse Konstanten wie Dielektrizitätskonstante ε_i Brechungsindex n_i, Permeabilität μ_i u. s. w. charakterisiert werden, die sämtlich tensoriell der Partikel zugeteilt werden können. Ausser diesen üblichen Charakterisierungsgrössen wollen wir ein Leitvermögen der Partikel σ_i einführen, welches im allgemeinen Falle auch als anisotrop angenommen werden darf. Derartige Anisotropie dürfte bei gewissen in Schichtstruktur aufgebauten Partikeln vorkommen.

Zwecks leichterer Durchführbarkeit unserer Rechnungen wollen wir die Partikel als starr und rotationsellipsoidisch annehmen. Eine weitere Voraussetzung gehe dahin, dass die Hauptachsen für den Brechungsindex, die Dielektrizitätskonstante und das Leitvermögen mit dem geometrischen Achsen zusammenfallen.

Wir legen ein Koordinatensystem (1, 2, 3) längs der Achsen der Partikel und führen ferner ein raumfestes Koordinaten-

system (x, y, z) mit der y-Achse in der Richtung des Lichtstrahles und der z-Achse parallel zum Felde ein.

Da gemäss der anfangs gemachten Voraussetzung die Messungen in einem sinusförmigen Wechselfelde vorgenommen werden sollen, führen wir direkt dessen Frequenz ω ein: weiterhin benutzen wir für die nachfolgenden Rechnungen die komplexe Dielektrizitätskonstante

$$\bar{\varepsilon}_i = \varepsilon_i - j\frac{4\pi\sigma_i}{\omega} \quad (i = 1, 2, 3) j = \sqrt{-1} \qquad (1)$$

und setzen für die Dielektrizitätskonstante des Mediums

$$\bar{\varepsilon}_0 = \varepsilon_0 - j\frac{4\pi\sigma_0}{\omega} \qquad (2)$$

Das Ellipsoid befinde sich in einem homogenen elektrischen Wechselfelde $E = E_0 \cos \omega t$.

Die mathematische Behandlung wird wesentlich durch die gemachte Voraussetzung vereinfacht, dass die Partikel Rotationssymmetrie besitze. Demnach setzen wir $\bar{\varepsilon}_2 = \bar{\varepsilon}_3$. Dann lässt sich die Orientierung der Molekel vollständig durch die Richtung der Hauptachse (1) ausdrücken; das Problem ist zweidimensional. Die Hauptachse (1) des Rotationsellipsoides bildet mit dem elektrischen Feld einen Winkel ϑ. Wird nun das Feld als quasistationär betrachtet, so erhält man nach Björnståhl (1) durch Erweiterung eines Ansatzes von Gans (2) für das Moment längs der Richtung i

$$f_1 = \frac{\bar{\varepsilon}_0(\varepsilon_1' - 1)}{4\pi + (\varepsilon_1' - 1)P} v E_1;$$

$$f_2 = \frac{\bar{\varepsilon}_0(\varepsilon_2' - 1)}{4\pi + (\varepsilon_2' - 1)P} v E_2; \qquad \text{mit } \varepsilon_i' = \frac{\bar{\varepsilon}_i}{\bar{\varepsilon}_0} \qquad (3)$$

wo v das Volumen des Ellipsoides ist und P von der Form gemäss

$$P = \frac{4\pi(1-e^2)}{e^2}\left\{\frac{1}{2e}\ln\frac{1+e}{1-e} - 1\right\} \text{ für gestreckte Ellipsoide, und}$$

$$P = \frac{4\pi}{e^2}\left\{1 - \frac{\sqrt{1-e^2}}{e}\ \text{arc sin}\ e\right\} \text{ für abgeplattete Ellipsoide,} \quad (4)$$

$$P + 2P' = 4\pi$$

abhängt. e ist die Exzentrizität des Ellipsoides. Für das Feld in den verschiedenen Richtungen finden wir

$$\begin{aligned} E_1 &= E\cos\vartheta = E_0\cos\omega t\cos\vartheta; \\ E_2 &= -E\sin\vartheta = -E_0\cos\omega t\sin\vartheta \end{aligned} \quad (5)$$

und für die Momente längs der Achsen

$$f_1 = v E_0 (a' + b' j)\cos\vartheta\cos\omega t \quad = \frac{v E_0 a'}{\cos\delta}\cos\vartheta\cos(2\omega t + \delta) \quad (6)$$

$$f_2 = -v E_0 (c' + d' j)\sin\vartheta\cos\omega t = -\frac{v E_0 c'}{\cos\varepsilon}\sin\vartheta\sin(2\omega t + \varepsilon)$$

mit

$$\begin{aligned} &\text{tg}\,\delta = b'/a'; \qquad \text{tg}\,\varepsilon = d'/c' \\ &a' + b' j = \frac{\bar{\varepsilon}_0(\varepsilon_1' - 1)}{4\pi + (\varepsilon_1' - 1)P}; \quad c' + d' j = \frac{\bar{\varepsilon}_0(\varepsilon_2' - 1)}{4\pi(\varepsilon_2' - 1)P}. \end{aligned} \quad (7)$$

Jetzt können wir das auf die Partikel wirkende Drehmoment berechnen und finden folgenden Ausdruck für das momentane Drehmoment

$$M = -\frac{E_0^2 v}{4\pi}\sin 2\vartheta\left\{-a' + c' - \frac{a'}{\cos\delta}\cos(2\omega t + \delta) + \right.$$

$$\left. + \frac{c'}{\cos\varepsilon}\cos(2\omega t + \varepsilon)\right\}. \quad (8)$$

In unserem variablen Felde bildet sich keine konstante Verteilung aus, indes können wir beim Aufsuchen der Verteilungsfunktion ϱ von der allgemeinen Diffusionsgleichung ausgehen,

$$\frac{\partial\varrho}{\partial t} = D\,\Delta\varrho - \text{div}\,\varrho\,W \quad (9)$$

wo D die Rotationsdiffusionskonstante und W die Winkelgeschwindigkeit einer Partikel unter Einwirkung des Feldes ist.

Gleichung (9) können wir für unseren Fall schreiben

$$\frac{\partial \varrho}{\partial t} = \frac{D}{\sin \vartheta} \cdot \frac{\partial}{\partial \vartheta} \left\{ \sin \vartheta \left[\frac{\partial \varrho}{\partial \vartheta} - \frac{\varrho M}{k T} \right] \right\}. \tag{10}$$

Der Ausdruck für M in Gleichung (8) ist ziemlich verwickelt; er lässt sich leichter übersehen, wenn wir setzen

$$A \cos (2 \omega t + \Delta) = - \frac{a'}{\cos \delta} \cos (2 \omega t + \delta) + \\ + \frac{c'}{\cos \varepsilon} \cos (2 \omega t + \varepsilon). \tag{11}$$

Daraus folgt

$$A \cos \Delta = - a' + c'$$

$$A \sin \Delta = a' \operatorname{tg} \delta - c' \operatorname{tg} \varepsilon$$

sowie weiter

$$A^2 = (c' - a')^2 + (a' \operatorname{tg} \delta - c' \operatorname{tg} \varepsilon)^2$$

$$\operatorname{tg} \Delta = \frac{a' \operatorname{tg} \delta - c' \operatorname{tg} \varepsilon}{c' - a'}; \quad c' \neq a'$$

und

$$M = - \frac{E_0^2 v}{4} (\sin 2 \vartheta) (c' - a') \left\{ 1 + \frac{\cos (2 \omega t + \Delta)}{\cos \Delta} \right\}. \tag{12}$$

Einführung des Ausdruckes (12) in Gl. (10) ergibt

$$\frac{\partial \varrho}{\partial t} = \frac{D}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left\{ \left[\frac{\partial \varrho}{\partial \vartheta} + \varrho \varkappa \left(1 + \frac{\cos (2 \omega t + \Delta)}{\cos \Delta} \right) \sin 2 \vartheta \right] \sin \vartheta \right\} \tag{13}$$

mit

$$\varkappa = \frac{E_0^2 v}{4 k T} (c' - a').$$

Als Lösung können wir unter Hinblick auf den statistischen Fall in erster Näherung versuchsweise einen Ausdruck der Form

$$\varrho = \varrho_0 (1 + (3 \cos 2 \vartheta + 1) \psi)$$

verwenden, in welchem ψ eine Funktion von t und ϱ_0 die Verteilung ohne Feld ist, und erhalten

$$\frac{1}{D}\cdot\frac{d\psi}{dt}+6\psi=\varkappa\left\{1+\frac{\cos(2\omega t+\Delta)}{\cos\Delta}\right\}. \tag{14}$$

Eine Auflösung dieser Gleichung ergibt sich aus

$$\psi=\frac{1}{6}\varkappa\{1+B\cos(2\omega t+\varphi)\}$$

wo

$$B=\frac{\cos\eta}{\cos\Delta};\quad \varphi=\Delta-\eta;\quad \operatorname{tg}\eta=\frac{\omega}{3D}.$$

Der Schlussausdruck für die Verteilungsfunktion wird also in erster Näherung

$$\varrho=\varrho_0\left\{1+\frac{E_0^2 v}{24kT}(c'-a')\cdot\right.$$
$$\left.\cdot\left\{1+\frac{\cos\eta}{\cos\Delta}\cos(2\omega t+\Delta-\eta)\right\}(3\cos 2\vartheta+1)\right\} \tag{15}$$

wo

$$\operatorname{tg}\eta=\frac{\omega}{3D};\quad \operatorname{tg}\Delta=\frac{a'\operatorname{tg}\delta-c'\operatorname{tg}\varepsilon}{a'-c'}.$$

Da für die weitere Berechnung des elektrooptischen Effektes sich durch die Einführung der Zeitabhängigkeit gegen den statistischen Fall nichts ändert, weil die Winkelabhängigkeit dieselbe ist, kann dieser Teil des Problems genau so behandelt werden wie beim statistischen Falle. Wir werden deshalb die Durchführung nicht im einzelnen erörtern.

Aus der Zeitabhängigkeit ergibt sich hier die momentane Doppelbrechung und damit folgender Ausdruck für die Differenz des Brechungsindex zwischen den Richtungen z parallel zum Felde und x senkrecht zum Felde und dem Strahlenwege

$$\left(\frac{n_z-n_x}{n_0}\right)_{\text{mom.}}=\frac{2\pi N v^2 E_0^2}{30kT}(c'-a')\cdot$$
$$\cdot\left\{1+\frac{\cos\eta}{\cos\Delta}\cos(2\omega t+\Delta-\eta)\right\}(h-h')^R \tag{16}$$

N bedeutet darin die Anzahl Partikeln pro Volumeneinheit.

Der Ausdruck $h-h'$ ist an Form und optische Eigenschaf-

ten der Partikel und an die optischen Eigenschaften des Lösungsmittels gebunden. Betreffs näherer Erörterung seiner Bedeutung s. Snellman und Björnståhl (3).

E_0 ist die bei sinusförmigem Strom durch die Gleichung $E_0 = E_{\text{eff}} \sqrt{2}$ mit der Messpannung verknüpfte maximale Feldstärke.

Wie man sieht, setzt sich der Ausdruck (16) aus einem zeitabhängigen und einem zeitunabhängigen Teile zusammen; beide hängen, wie wir bald sehen werden, von der Frequenz ab.

Im allgemeinen ist A eine kleine Grösse, und der Term mit ωt beträgt deshalb gewöhnlich weniger als 1. Dann ist die Doppelbrechung während der ganzen Periode positiv, pendelt jedoch zwischen gewissen Werten.

Die gemessene Doppelbrechung wird abhängig von der Messmethode. Bestimmt man sie nach einem stroboskopischen Verfahren, so wird man trotz Abwesenheit eines festen Dipolmomentes Relaxationsphänomene beobachten. Dieser Unterschied gegenüber Messungen der Dielektrizitätskonstanten hat seinen Grund in der Notwendigkeit, hier höhere Terme mit in Betracht zu ziehen.

Bei den Messungen an Kolloiden ist keine stroboskopische Methode zur Anwendung gekommen, man hat vielmehr okular abgelesen. Dabei erstreckt sich die Ablesung über einen gewissen Zeitmittelwert, falls die Frequenz so gross ist, dass Talbots Gesetz gilt, d. h. dass sie die Verschmelzungsfrequenz übersteigt. Man kann zeigen, dass unter solchen Umständen der kompensierte Teil gleich dem zeitunabhängigen Teile ist.[1] Diese Doppelbrechung ist also

$$\frac{n_z - n_x}{n_0} = \frac{2\pi N v^2 E_{\text{eff}}^2}{15kT}(h - h')^R \{c' - a'\}. \qquad (17)$$

Der Term $(c' - a')$ ist in manchen Fällen frequenzabhängig; seine nähere Diskussion ist also von Interesse.

a' resp. c' stellen die reellen Teile in den Ausdrücken (7) dar.

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[1] Die Relaxation des Verschiebungsanteiles tritt also bei dieser Methode der Doppelbrechungsmessung nicht auf, jedoch verursacht ein festes Dipolmoment dabei Relaxation.

Für diese finden wir

$$\begin{aligned} 4\pi(X_1^2 + Z_1^2)\,a' &= \varepsilon_0(\varepsilon_1 - \varepsilon_0)\,X_1 - a_0(a_1 - a_0)\,X_1 + \\ &\quad + \varepsilon_0(a_1 - a_0)\,Z_1 + a_0(\varepsilon_1 - \varepsilon_0)\,Z_1 \\ 4\pi(X_2^2 + Z_2^2)\,c' &= \varepsilon_0(\varepsilon_2 - \varepsilon_0)\,X_2 - a_0(a_2 - a_0)\,X_2 + \\ &\quad + \varepsilon_0(a_2 - a_0)\,Z_2 + a_2(\varepsilon_2 - \varepsilon_0)\,Z_2 \end{aligned} \tag{18}$$

mit folgenden Abkürzungen

$$\begin{aligned} &X_1 = \varepsilon_0 + (\varepsilon_1 - \varepsilon_0)\,A;\quad Z_1 = a_0 + (a_1 - a_0)\,A; \\ &\qquad\qquad a_i = \frac{4\pi\sigma_i}{\omega}\,(i = 0,1,2) \\ &X_2 = \varepsilon_0 + (\varepsilon_2 - \varepsilon_0)\,B;\quad Z_2 = a_0 + (a_2 - a_0)\,B; \\ &\qquad A = P/4\pi;\quad B = P'/4\pi \end{aligned} \tag{19}$$

so dass sich für die allgemeine Formel folgende Beziehungen ergeben

$$\begin{aligned} &4\pi(c' - a')(X_1^2 + Z_1^2)(X_2^2 + Z_2^2) = -\varepsilon_0(\varepsilon_1 - \varepsilon_0)\,X_1(X_2^2 + Z_2^2) + \\ &+ \varepsilon_0(\varepsilon_2 - \varepsilon_0)\,X_2(X_1^2 + Z_1^2) - \varepsilon_0(a_1 - a_0)\,Z_1(X_2^2 + Z_2^2) + \\ &+ \varepsilon_0(a_2 - a_0)\,Z_2(X_1^2 + Z_1^2) - a_0(a_2 - a_0)\,X_2(X_1^2 + Z_1^2) + \\ &+ a_0(a_1 - a_0)\,X_1(X_2^2 + Z_2^2) - a_0(\varepsilon_1 - \varepsilon_0)\,Z_1(X_2^2 + Z_2^2) + \\ &+ a_0(\varepsilon_2 - \varepsilon_0)\,Z_2(X_1^2 + Z_1^2). \end{aligned} \tag{20}$$

Diese Formel is im entwickelten Zustand schwer zu übersehen und lässt sich in dieser Gestalt nicht diskutieren. Wir begnügen uns mit Erörterung einiger in der Praxis möglicherweise vorkommender Fälle.

Zunächst sehen wir nach, was sich ergibt, wenn die Frequenz im Verhältnits zum Leitvermögen gross ist, d. h. $a_i = 0$; $Z_i = 0$

$$4\pi(a' - c') = \frac{\varepsilon_0(\varepsilon_1 - \varepsilon_2) + (\varepsilon_1 - \varepsilon_0)(\varepsilon_2 - \varepsilon_0)(B - A)}{\varepsilon_0\left[1 + \frac{\varepsilon_1 - \varepsilon_0}{\varepsilon_0}A\right]\left[1 + \frac{\varepsilon_2 - \varepsilon_0}{\varepsilon_0}B\right]}. \tag{21}$$

Dies ist derselbe Ausdruck, den man für eine Partikel mit schwacher Leitfähigkeit in einer isolierenden Flüssigkeit erhält.

Die für diesen Fall abgeleiteten Beziehungen können somit als Grenzfall des von uns gewonnenen Ausdrucks aufgefasst werden.

Das Vorzeichen der in diesem Falle zu erwartenden Doppelbrechung hängt auch von dem Term $h - h'$ ab. In den allgemeinen Fällen, wo auch Absorption stattfindet, ergeben sich Formeln, aus denen das Vorzeichen der Doppelbrechung schwer zu entnehmen ist.

Für die übrigen Fälle kann man sagen, dass, wenn die Partikeln aus isotroper Substanz bestehen, die Doppelbrechung, falls sie vorhanden ist, unabhängig von der Form mit positivem Vorzeichen auftritt, dass dagegen bei anisotroper Substanz je nach Umständen positive oder negative Doppelbrechung auftreten kann.

Bei den übrigen noch zu erörternden Fällen können wir im allgemeinen von der Leitfähigkeit des Lösungsmittels absehen, da dieses in den meisten Fällen höchstens aus einer äusserst schwachen Salzlösung besteht.

Wir können also in Gl. (20) setzen $a_0 = 0$

$$4\pi(c'-a')(X_1^2+A^2a_1^2)(X_2^2+B^2a_2^2)=\varepsilon_0^2(\varepsilon_1-\varepsilon_0)X_1(X_2^2+B^2a_2^2)- \tag{22}$$
$$-\varepsilon_0(\varepsilon_2-\varepsilon_0)X_2(X_1^2+A^2a_1^2)+\varepsilon_0a_1^2A(X_2^2+B^2a_2^2)-\varepsilon_0a_2^2B(X_1^2+A^2a_1^2).$$

Der erste zu besprechende Fall betrifft das Verhalten der Metallkolloide.

Diese kolloidalen Partikeln haben grosses, nicht anisotropes Leitvermögen. In erster Näherung darf man wohl auf der rechten Seite gegenüber dem Term $\varepsilon_0 a' A B(B-A)$ die übrigen vernachlässigen und erhält dann

$$4\pi(c'-a')=\frac{\varepsilon_0(B-A)}{AB}. \tag{23}$$

Die Einstellung der Partikeln hängt nicht von Frequenz und Leitvermögen ab, sondern lediglich von der Form. Ein gestrecktes Rotationsellipsoid stellt sich mit der Hauptachse längs des Feldes ein, ein abgeplattetes mit der Hauptachse senkrecht zu diesem.

Das Vorzeichen der Doppelbrechung wird auch von dem

optischen Faktor $h - h'$ mitbestimmt. In diesem Falle ist gleiches Vorzeichen für die Doppelbrechung zu erwarten wie für die Strömungsdoppelbrechung, was in der Tat eintrifft.

Versuche, aus denen die Unabhängigkeit von der Frequenz hervorgeht, liegen nicht vor. Bei niedrigen Frequenzen dürften auch Anomalien vorkommen und die Messungen erschweren. So beobachtete Kruyt (4) an Goldkolloiden im elektrischen Felde die Bildung von perlbandähnlichen Ketten.

Es könnte scheinen, als ob man lediglich bei Metallkolloiden auf die Leitfähigkeitsterme Rücksicht zu nehmen brauchte, doch ist dies wohl nicht der Fall.

Bei Messungen der Dielektrizitätskonstanten gemachte Erfahrungen machen es wahrscheinlich, dass die Leitfähigkeitsterme in einer ganzen Reihe anderer Fälle beachtet werden müssen. Untersuchungen über die Dielektrizitätskonstanten von u. a. Vanadinpentoxydsolen und gewissen Farbstoffen in wässriger Lösung haben für diese Kolloide Dielektrizitätskonstanten bis zum fünffachen Betrage von der des Wassers ergeben.

Errera (6), der Vanadinpentoxydsole gemessen hat, versuchte die Ergebnisse durch die Annahme einer Seignettesalzähnlichen Struktur der Partikeln zu deuten. Dagegen spricht jedoch der Umstand, dass in fester Form die Dielektrizitätskonstante erheblich kleiner ist ($\varepsilon \sim 10$). Wohl aber könnte man das Resultat aus Anisotropie der Leitfähigkeit erklären.[1]

Zu derselben Gruppen sind auch Bentonit und Viruslösung sowie gewisse Farbstoffe zu rechnen.

Es lässt sich zeigen, dass die hier entwickelten Ansätze zu hinsichtlich der Grössenordnung besser stimmenden Werten führen, ohne dass deswegen die Leitfähigkeit unnatürlich gross zu sein braucht. Es sei deshalb der elektrooptische Effekt für einige Fälle diskutiert, in denen die Leitfähigkeit anisotrop ist.

Wir setzen in Gleichung (22) $a_1 = 0$ und erhalten

$$4\pi(c'-a')\,X_1^2(X_2^2+B^2a_2^2) = \varepsilon_0(\varepsilon_1-\varepsilon_0)\,X_1(X_2^2+B^2a_2^2) - \\ -\varepsilon_0(\varepsilon_2-\varepsilon_0)\,X_2\,X_1^2-\varepsilon_0\,a_2^2\,B\,X_1^2. \tag{24}$$

[1] Szegvari und Wigner (5) haben auch die Unwahrscheinlichkeit des Vorkommens von festen Dipolen in den Partikeln aufgezeigt.

Nun möge bei niederen Frequenzen der Leitfähigkeitsterm dominieren; es folgt

$$4\pi(c'-a')\,X_1^2\,B^2\,a_2^2=\varepsilon_0(\varepsilon_1-\varepsilon_0)\,X_1\,B^2\,a_2^2-\varepsilon_0\,a_2^2\,B\,X_1^2$$

und

$$4\pi(c'-a')=\frac{\varepsilon_0}{B\,X_1}\{(\varepsilon_1-\varepsilon_0)(B-A)-\varepsilon_0\}. \qquad (25)$$

Hier stellt sich die Partikel unabhängig von der Frequenz ein. Für wässrige Lösungen können wir meist $\varepsilon_0>\varepsilon_1$ annehmen.

Bei gestreckten Partikeln $(A<B)$ erfolgt dann die Einstellung in der Regel mit der Hauptachse senkrecht zum Felde: bei abgeplatteten Rotationsellipsoiden $(A>B)$ liegt die Relationsachse in der Feldrichtung, wenn $(\varepsilon_0-\varepsilon_1)(B-A)>\varepsilon_0$. (Bei dünnen scheibenförmigen Partikeln steht die Hauptachse normal zum Felde).

Bei höheren Frequenzen überwiegt der Leitfähigkeitsterm nicht; man erhält dann einen Übergang zu der dielektrisch zu erwartenden Einstellung. Herrscht der Term a_2 nicht mehr vor, so beginnt die Einstellung von dem Term

$$\frac{\varepsilon_0}{X_1\,X_2}\{(\varepsilon_1-\varepsilon_2)\,\varepsilon_0-(\varepsilon_1-\varepsilon_0)(\varepsilon_2-\varepsilon_0)(B-A)\} \qquad (26)$$

abhängig zu werden. Hier spielt auch die Dielektrizitätskonstante in der Richtung (2) eine Rolle. Haben die beiden Terme (25) und (26) verschiedene Vorzeichen, so ist hier auch eine Inversion denkbar.

Setzt man in Gleichung (22) $a_2=0$, so ergibt sich bei Vorherrschen des Leitfähigkeitsterms

$$4\pi(c'-a')=\frac{\varepsilon_0}{A\,X_2}\{\varepsilon_0+(\varepsilon_2-\varepsilon_0)(B-A)\}. \qquad (27)$$

Auch hier wird in einem grossen Gebiete die Einstellung unabhängig von der Frequenz.

Ebenso wie oben finden wir für gestreckte Partikeln $[(A<B)$ und $(\varepsilon_2<\varepsilon_0)]$ in der Regel Einstellung mit der Hauptachse parallel zum Felde; bei einem abgeplatteten Ellipsoid ist

$[(A > B)$ und $(\varepsilon_2 < \varepsilon_0)]$ und die Einstellung erfolgt mit der Hauptachse normal zum Felde.

Es ergibt sich also, dass die Einstellung der Kolloidpartikel in einem grossen Intervall von der Frequenz unabhängig sein soll. Doch beginnt bei höheren Frequenzen der Term der Dielektrizitätskonstante vorzuherrschen, und dann ist eine Änderung von Grösse und eventuell auch Richtung der Einstellung zu erwarten, je nachdem, wie sich die Anisotropie der Dielektrizitätskonstanten der Partikel verhält.

Die Formeln vermögen ohne weiteres Erreras (7) Resultate der Doppelbrechungsmessungen von Paraazoxyphenetol und Benzopurpurin zu erklären. Er fand dabei die Doppelbrechung, in einem grossen Gebiete mit vermutlich überwiegendem Leitfähigkeitsterm, unabhängig von der Frequenz; später bei etwa 10^6 Hz (Hertz) begann sie abzunehmen und kehrte ihr Vorzeichen bei etwa 10^7—10^8 Hz um von negativ in positiv bei Benzopurpurin und umgekehrt bei Paraazoxyphenetol.[1]

Schwieriger liegen die Verhältnisse bei Vanadinpentoxyd, wo die Dispersion ein Minimum bei 10^3 Hz und ein Maximum bei 10^6 Hz durchläuft und sodann abfällt. Negative Doppelbrechung wurde jedoch nicht wahrgenommen.

Nach Erreras Annahme sollte die Doppelbrechung sich aus einem positiven und einem negativen Teile zusammensetzen. Der positive war frequenzunabhängig bis 10^7 Hz, was mit den von uns entwickelten Vorstellungen stimmt; der negative war am grössten bei 10^3—10^4 Hz, nahm dann ab und verschwand bei 10^7 Hz.

Die Verhältnisse lassen sich vielleicht durch die Annahme der Existenz von zwei Partikelarten erklären. Der negative Anteil würde dann von Partikelkonglomeraten anderer Form und ev. mit anderen elektrischen und optischen Eigenschaften herstammen.

Eine Stütze für eine solche Deutung gewährt möglicherweise Zochers (9) ultramikroskopische Beobachtung der Einstellung von Vanadinpentoxyd im elektrischen Felde. Während der

[1] Das positive Vorzeichen von Paraazoxyphenetol steht im Widerspruch zu Björnståhls (8) Feststellung negativer Doppelbrechung in diesen Lösungen. Die Strömungsdoppelbrechung gibt auch nach Snellman und Björnståhl (3) negative Doppelbrechung.

Hauptteil der Partikeln sich parallel zum Felde einstellte, waren auch Partikelgruppen mit senkrechter Einstellung zum Felde vorhanden.

Man muss annehmen, dass dieselben Effekte auch an den Anomalien der Doppelbrechungsverhältnisse von Bentonit (10) und Virussolen (11) beteiligt sind. Bei niedrigen Frequenzen und geringen Feldstärken zeigen diese Sole mit Zunahme der Feldstärke eine Inversion der Doppelbrechung von negativ zu positiv. Bei höheren Frequenzen tritt diese Anomalie nicht auf und, was wichtig ist, in höherer Konzentration nur nahe dem taktoiden Zustande. Die Kurven lassen sich damit erklären, dass eben entstehende taktoide Gruppen sich bei niedrigen Frequenzen, wo der Leitfähigkeitsterm überwiegt, mit zunehmendem Felde rasch auf Sättigung einstellen. Bei etwas höheren Frequenzen verliert der Leitfähigkeitsterm an Bedeutung und infolgedessen kann Vorzeichenänderung der Doppelbrechung eintreten.

Zum Schlusse darf vielleicht hervorgehoben werden, dass, abgesehen von den hier besprochenen Effekten, in gewissen Fällen die Möglichkeit des Bestehens eines Effektes vorliegt, der Ähnlichkeit mit dem eines permanenten Dipols hat.

Es lässt sich denken, dass bei der Ionenverschiebung der Partikeln in einem Wechselfelde es für die Partikel leichter ist umzuschlagen als dass die Ionen sich zurückbewegen. Da die Partikel in solchen Fällen sich so verhält, als wenn sie ein festes Moment hätte, so muss dabei auch ein Relaxationseffekt in Erscheinung treten, und zwar bei recht niedrigen Frequenzen. Es ist zu beachten dass eine solche Relaxation auch bei Doppelbrechungsmessungen ohne stroboskopische Methode bemerkt wird.

Versuche, die sich gemäss einer derartigen Überlegung deuten lassen, liegen jedoch nicht vor.

Zusammenfassung.

Es wurde eine theoretische Behandlung der Orientierung bei elektrischer Doppelbrechung gegeben, welche auch Rücksicht auf das Leitvermögen der Partikeln nimmt. Sie setzt voraus, dass ein Wechselfeld angelegt ist.

Die Theorie für nichtleitende Flüssigkeiten ist ein Grenzfall der allgemeinen Theorie leitender Flüssigkeiten.

Die Möglichkeit der Erklärung von gewissen gefundenen elektrooptischen Effekten durch diese Theorie wird dargelegt.

Die Untersuchungen sind mit Unterstützung von der Rockefellerstiftung ausgeführt.

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Some Aspects of Preparative Electrophoresis.

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The electrochemical methods for the fractionation of high molecular compounds proceed essentially along two different lines. One employs a series of compartments separated by vertical membranes, each compartment being stirred; the other is the moving boundary method in a vertical U-tube, where stirring or convection must not take place. Much attention has been paid in the past few years to both methods. The membrane method has been studied and developed recently by Du Vigneaud *et al.* (1), Tiselius (2), Hahn and Tiselius (3), Spies *et al.* (4), Gutfreund (5), and others. The method of regulating pH, presented in (3), is especially noteworthy, as it makes possible the attainment of a more even distribution of the potential gradient over all the cells. Otherwise almost the whole potential drop tends to localize itself in the middle compartment, while only weak electrical fields are established in the other compartments.

The moving boundary method was first used for a preparative purpose by Bennhold (6), and since then the method has been much refined especially by Tiselius (7). Efforts to raise the separation speed by building special preparative apparatus have been made by Tiselius (8) and the present author (9). The preparative apparatus of Theorell (10) is something between a moving boundary and a membrane apparatus.

The membrane method is much superior to the moving boundary method as regards separation speed and simplicity of the technical arrangements, but the latter method is superior with respect to the purity of the isolated substance. If the mixture to be separated contains a small number of well defined

electrochemical components, the moving boundary method will in general be able to give fractions of nearly absolute purity, provided that the experiment is well conducted with the aid of optical control of the boundaries, which is possible with the apparatuses now in use. It is therefore important to raise the separation speed as much as possible even in this method. The factors which influence the efficiency of the procedure are: 1) the concentration of the component to be isolated; 2) the mobility difference between that and the subsequent component; 3) the current density; 4) the conductivity; 5) the construction of the U-tube; 6) the temperature; 7) the diffusion. This article will attempt to discuss, with the aid of mathematical treatment where possible, the influence of these different factors upon the separation speed in the moving boundary method.

Let us suppose we have to separate a substance with the mobility $u + \Delta u$ from another with the mobility u. The relative velocity between the boundaries is

$$\frac{\Delta u i}{\varkappa}, \tag{1}$$

where i is the current density and $\varkappa$ the conductivity. If we multiply by the concentration C of the substance that is to be isolated and by the cross-sectional area q of the U-tube, we have the separation speed:

$$W = \frac{C \Delta u i q}{\varkappa} \tag{2}$$

in weight units or moles per volume unit.

In this equation all variables are not mutually independent, the current density being limited by the requirement that the heat production in the tube must not exceed a certain value, above which convections set in and render all observations impossible. Thus there is a connection between i and the other variables. To derive this it is necessary to study the stationary thermal condition in a tube through which a current is passing.

Elementary mathematical theory gives for a cylindrical tube the differential equation:

$$r\frac{d^2t}{dr^2}+\frac{dt}{dr}+\frac{\varepsilon r i^2}{\varkappa k_s}=0 \tag{3}$$

for the temperature distribution in the solution and

$$r\frac{d^2t}{dr^2}+\frac{dt}{dr}=0 \tag{4}$$

for the glass wall. Here t is the temperature, r the distance from the axis of the tube, ε the electrical heat equivalent, and k_s the thermal conductivity of the solution. In the equation (3) the last term is not constant as both the current density and the conductivities vary with temperature. i and $\varkappa$ vary proportionately, however, so we need only consider the variation of i/k_s. This is not very large, since both i and k_s rise with temperature, and the integration of the differential equation as if the last term were constant will give a quite good approximation of the true heat distribution; the integration gives:

$$t=t_{R+a}+\frac{\varepsilon i^2R^2}{2\varkappa k_g}\ln\frac{R+a}{R}+\frac{\varepsilon i^2}{4\varkappa k_s}(R^2-r^2)=t_0-\frac{\varepsilon i^2r^2}{4\varkappa k_s} \tag{5}$$

for the solution and

$$t=t_{R+a}+\frac{\varepsilon i^2R^2}{2\varkappa k_g}\ln\frac{R+a}{r} \tag{6}$$

for the wall. R is the internal radius of the tube and a the thickness of the wall. In (5) t_{R+a} is the thermostat temperature. The second term indicates the temperature increase over the wall, and the last term describes how the temperature rises in the solution itself. k_g is the heat conductivity of the glass, and t_0 is the temperature in the centre of the tube.

The factor decisive for a convection-free electrophoresis is not the temperature variations, but the variations of density. The greatest temperature difference within the tube is, according to (5),

$$t_0-t_R=\frac{\varepsilon i^2R^2}{4\varkappa k_s}. \tag{7}$$

The corresponding difference of density is, if the density is written as a function $\varrho=\varrho(t)$ of the temperature,

$$\varrho_0 - \varrho_R = \frac{\varepsilon i^2 R^2}{4 \varkappa k_s} \varrho'(t_1), \tag{8}$$

where t_1 is the temperature at a point between 0 and R. The difference of density thus diminishes with the density derivative $\varrho'(t_1)$. Now water has a density curve which passes through a maximum at + 4° C, where thus $\varrho'(t) = 0$. This happy circumstance was, as is known, made use of by TISELIUS in his apparatus constructed in 1937. This was in fact one of the greatest improvements in this construction, and no factor has played such an important part in increasing the separation speed as the method of working at the density maximum of water. The striking effect of this has been shown by LONGSWORTH and MACINNES (11) by the application of eq. (5) to a cylindrical U-tube and by diagrams showing the density progress within the tube for various temperatures. They point out in the same paper that the temperature of maximum density is affected by substances dissolved in the water, a factor that should be taken into account in electrophoretical work. As yet, however, we have not complete knowledge of the influence of the common buffer salts in this respect. That high concentrations of urea radically change the density curve has recently been shown by MOORE (12).

In the following we suppose that the electrophoresis progresses near the density maximum, and that consequently $t_0 > t_m > t_R$, where t_m is the temperature for maximum density. The equation (8) is now no longer useful, partly because $\varrho_0 - \varrho_R$ is no longer the greatest difference of density in the tube, and partly because the derivative $\varrho'(t_1)$ can equal 0.

The greatest density difference in the tube may not either be identical with the quantity which is directly decisive for whether convections appear or not. According to the author's opinion the derivative $\frac{d\varrho}{dr}$ may rather be the most adequate mathematical expression for this quantity. Consequently we claim that this derivative must nowhere in the tube exceed a certain critical value, $\left(\frac{d\varrho}{dr}\right)_m$.

The density is a quadratic function of the temperature and may be written:

$$\varrho - \varrho_m = - c\,(t - t_m)^2, \tag{9}$$

where ϱ_m is the density maximum. According to (5), the temperature is in its turn a quadratic function of r, and the density is therefore a biquadratic function of r:

$$\varrho - \varrho_m = - c \left[t_0 - t_m - \frac{\varepsilon\, i^2\, r^2}{4\, \varkappa\, k_s} \right]^2. \tag{10}$$

The derivative to be examined is:

$$\frac{d\,\varrho}{d\,r} = \frac{c\,\varepsilon\, i^2}{\varkappa\, k_s} \left[(t_0 - t_m)\, r - \frac{\varepsilon\, i^2\, r^3}{4\, \varkappa\, k_s} \right]. \tag{11}$$

It is consequently of the third degree of r, and its progress is roughly the following. In the centre of the tube it is 0, then rises to a maximum at the point

$$r = \frac{1}{i} \sqrt{\frac{4\, \varkappa\, k_s\, (t_0 - t_m)}{3\, \varepsilon}}, \tag{12}$$

then falls again to 0 at the point

$$r = \frac{1}{i} \sqrt{\frac{4\, \varkappa\, k_s\, (t_0 - t_m)}{\varepsilon}}, \tag{13}$$

afterwards assuming increasing negative values till $r = R$.

We obtain the maximum of the density derivative by insertion of (12) in (11):

$$\left(\frac{d\,\varrho}{d\,r} \right)_{\text{max.}} = \frac{4\, c}{3\, \sqrt{3}} \sqrt{\frac{\varepsilon}{\varkappa\, k_s}}\, i\, (t_0 - t_m)^{3/2}, \tag{14}$$

and its minimum by putting $r = R$ in (11):

$$\left(\frac{d\,\varrho}{d\,r} \right)_{\text{min.}} = \frac{c\,\varepsilon\, i^2}{\varkappa\, k_s} \left[(t_0 - t_m)\, R - \frac{\varepsilon\, i^2\, R^3}{4\, \varkappa\, k_s} \right]. \tag{15}$$

The most favourable temperature distribution is that which makes these two numerically equal, but with opposite signs. We consequently get the equation:

$$\frac{4c}{3\sqrt{3}}\sqrt{\frac{\varepsilon}{\varkappa k_s}}\,i\,(t_0-t_m)^{3/2}=-\frac{c\,\varepsilon\,i^2}{\varkappa k_s}\left[(t_0-t_m)\,R-\frac{\varepsilon i^2 R^3}{4\varkappa k_s}\right]. \quad (16)$$

With a new variable:

$$z=\sqrt{\frac{\varkappa k_s (t_0-t_m)}{\varepsilon i^2 R^2}} \quad (17)$$

equation (16) may be reduced to:

$$\frac{4}{3\sqrt{3}}z^3+z^2-\frac{1}{4}=0. \quad (18)$$

Its roots are:

$$z_1=z_2=-\frac{\sqrt{3}}{2} \quad \text{and} \quad z_3=\frac{\sqrt{3}}{4}. \quad (19)$$

Of these only the positive one is physically practicable. We consequently have:

$$t_0-t_m=\frac{3\,\varepsilon\,i^2 R^2}{16\,\varkappa k_s}. \quad (20)$$

If this is inserted in (14), we have an equation which we solve explicitly for i:

$$i=2\sqrt[4]{\frac{\varkappa^2 k_s^2}{c\,\varepsilon^2 R^3}\left(\frac{d\,\varrho}{d\,r}\right)_m}. \quad (21)$$

Here we have an expression for the maximum current density as a function of the greatest permitted density derivative and the variables previously introduced. The insertion of this expression in (2) finally gives us the separation speed for the cylindrical U-tube:

$$W=2\,\pi\,C\,\Delta u\sqrt{\frac{k_s}{\varkappa\,\varepsilon}}\sqrt[4]{\frac{1}{c}\left(\frac{d\,\varrho}{d\,r}\right)_m}R^{5/4}, \quad (22)$$

or, with the introduction of a new constant:

$$W=K\,C\,\Delta u\,\varkappa^{-\frac{1}{2}}R^{\frac{5}{4}}. \quad (23)$$

If we choose instead, as did Tiselius, a rectangular U-tube, the equations become somewhat different. If we neglect the

heat conduction through the short walls, we obtain for the solution the differential equation:

$$\frac{d^2 t}{d r^2} + \frac{i^2}{\varkappa k_s} = 0, \tag{24}$$

and for the wall:

$$\frac{d^2 t}{d r^2} = 0. \tag{25}$$

Here r represents the distance from the middle of the tube perpendicular to the long walls. If as before we integrate, supposing that the last term in (24) is constant, we have the temperature distribution:

$$t = t_{d+a} + \frac{\varepsilon i^2 d a}{\varkappa k_g} + \frac{\varepsilon i^2}{2 \varkappa k_s}(d^2 - r^2) = t_0 - \frac{\varepsilon i^2 r^2}{2 \varkappa k_s} \tag{26}$$

for the solution and

$$t = t_{d+a} + \frac{\varepsilon i^2 r a}{\varkappa k_g} \tag{27}$$

for the wall. Here d means half of the internal dimension of the tube perpendicular to the long walls.

The equation (26) becomes identical with (5) if we substitute $2\varkappa$ for $4\varkappa$, provided that both equations are written in the forms using t_0. Thus we can derive the maximum current density for the rectangular U-tube by substituting $4\varkappa$ for $2\varkappa$ and R for d in (21):

$$i = \sqrt{2} \sqrt[4]{\frac{\varkappa^2 k_s^2}{c \varepsilon^2 d^3} \left(\frac{d \varrho}{d r}\right)_m}, \tag{28}$$

and the separation speed for the rectangular tube becomes:

$$W = 4 \sqrt{2}\, C \Delta u l \sqrt{\frac{k_s}{\varepsilon \varkappa}} \sqrt[4]{\frac{1}{c} \left(\frac{d \varrho}{d r}\right)_m} d, \tag{29}$$

or if all constants are united into one:

$$W = K' C \Delta u l \varkappa^{-\frac{1}{2}} d^{\frac{1}{4}}, \tag{30}$$

l being half the longer internal dimension of the tube.

A treatment of the convection currents in electrophoresis measurements was given in 1941 by Mooney (13). Unfortunately, this paper was not available to the author at the time of writing.

Inspection of the equations (22) and (30) leads to the following interesting results.

The separation speed varies inversely with the square root of the conductivity. For the cylindrical tube the separation speed rises as the power 5/4 of the radius, thus considerably less than the cross-sectional area and the volume, which increase as the square of the radius. For a rectangular tube the efficiency is proportional to the length of the cell, but only to the fourth root of its breadth.

The two types of tubes are equally efficient when the condition:

$$\pi^4 R^5 = 2^6 l^4 d \tag{31}$$

is fulfilled. Hence the ratio between the cross-sectional areas of the rectangular and the cylindrical tubes is found to be:

$$\frac{q_2}{q_1} = \frac{4 l d}{\pi R^2} = \sqrt[5]{\frac{\pi^3}{4}\left(\frac{d}{l}\right)^3}. \tag{32}$$

For a given separation speed the cross-sectional area thus varies as the power 3/5 of the ratio between breadth and length. In the Tiselius cell (7) $d/l = 0.12$ and q_2/q_1 becomes 0.42. In the apparatus described in (9) d/l is 0.06 and the corresponding q_2/q_1 value is 0.28. It is thus seen that the narrow rectangular tubes introduced by Tiselius are extremely favourable, only small volumes being necessary to attain a comparatively high separation speed.

On the other hand, if we put the cross-sectional areas equal for the two types:

$$\pi R^2 = 4 l d, \tag{33}$$

the separation speeds are

$$\frac{W_2}{W} = \sqrt[8]{\frac{4}{\pi^3}\left(\frac{l}{d}\right)^3}. \tag{34}$$

Thus, for a given cross-sectional area, the separation speed varies as the power 3/8 of the ratio l/d.

It is also possible to derive the optimal thermostat temperature by the above method. We find the optimal temperature for the centre of the tube in equation (20), and with the aid of equations (5) and (26) the thermostat temperature is then easily calculated. If a rectangular U-tube is used, it becomes:

$$t = t_m - \frac{\varepsilon i^2 d^2}{\varkappa}\left[\frac{1}{8 k_s} + \frac{a}{d k_g}\right]. \qquad (35)$$

The variables in the final equations (22) and (29) are still not all mutually independent, but the relations which are to be found here are so complicated that it is of little value to attempt their expression in a mathematical form. Firstly, we have to consider the dependence of the mobilities, and then also that of Δu, on the salt concentration, which implies an indirect dependence of Δu on the conductivity. It is sufficient to say that Δu is a decreasing function of the salt concentration, and that the conductivity should consequently be kept low, for two reasons.

Furthermore, it should be pointed out that the variables refer to the moving layer and not to the solution with which the experiment is started. Owing to the boundary anomalies these layers are seldom equal either as to concentration or as to conductivity, and particularly not during preparative experiments, where considerable anomalies are as a rule permitted.

There are also other factors to be taken into consideration. A very important requirement is that the absolute velocity between the boundaries be as great as possible in comparison with the diffusion speed. The diffusion, which has not been taken into consideration hitherto, diminishes the yield of purified material. This demand is also best fulfilled by the narrow rectangular U-tube.

Finally, the boundary anomalies already mentioned are an important factor which must be known if it is desired to choose the most favourable experimental conditions. On the whole it may be said that the anomalies influence the rising

side favourably and the falling one unfavourably. The very complicated phenomena which are encountered in the case of boundary anomalies, and their influence upon the separation speed, will be discussed in more detail in another connection.

Summary.

1. The moving boundary method of electrophoretic fractionation is theoretically treated with regard to the separation speed.
2. By a mathematical analysis of the thermal stationary state in the U-tube the influence of conductivity and the form of the tube are derived. It is found that the rectangular form used by Tiselius is much superior to the cylindrical form, the separation speed per volume unit being much greater.
3. The optimal thermostat temperature is derived.
4. The influences of certain other factors, such as boundary anomalies, diffusion and salt concentration are briefly discussed.

The author is indebted to Professor Tiselius for interesting and helpful discussions.

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A Neutron Generator for Preparative Use.

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Artificial radioactive isotopes are being used to an increasing extent as indicators in the study of a number of important problems, mainly biological and chemical.

They may be prepared:

1) Directly, by a nuclear reaction brought about with ions of high velocity, usually deuterons.

2) Indirectly, by nuclear reactions caused by neutrons, formed in a nuclear process of type 1).

The direct method generally requires, if sufficient yields are to result, energies of the order of 10^6 eV. The indirect course, which was the first to be followed after the nuclear reaction

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \qquad (1)$$

had made a "natural" source of neutrons available, also provides a method for the artificial generation of radioactive isotopes at energies as low as the order of 100 keV. The nuclear reaction of type 1) that gives the largest yield in this case is (cf. 1):

$$^{2}_{1}\mathrm{D} + {}^{2}_{1}\mathrm{D} \longrightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \qquad (2)$$

At a deuteron energy of 200 keV, the use of this nuclear reaction can provide a neutron source corresponding to several grams of Rn + Be. The neutron radiation is practically monochromatic, with an energy of $2.3 \cdot 10^6$ eV.

In many investigations employing artificial radioactive indicators, an adequate activity is obtained in the final prepara-

tion with the help of a neutron source corresponding to only some tenths of a gram of Rn + Be. Consequently neutron generators built for potentials of the order of some hundreds of kV may have great practical importance in the preparative generation of isotopes, especially those with relatively short half-life periods, for example halogens, in the case of which transportation from a larger plant is quite impracticable.

In the present paper an apparatus will be described which has been constructed at this institute for the said purpose.

Most of the neutron generators that have been constructed have the ion source on the high-tension side and the target earthed to permit direct nuclear-physical measurements. In this case the construction has been simplified in that the ion source is at earth potential and hence the parts of the apparatus in this region need not be insulated against high tensions. In a preparative apparatus there is no impediment to placing the target at high tension, since this in no way hinders the necessary measurements of ionic current and neutron intensity.

A low-tension arc, mainly according to the design of Tuve, Dahl and Hafstad (2), has been chosen as the ion source [1][1]. The yield of atomic ions for this source is not as great as is usually the case for a canal ray tube, but, on the other hand, a higher total ionic current is obtained with a low-tension arc. Later improvements, carried out with ion sources of the low-tension type, have led to a considerable increased yield of atomic ions (3), so that this type of ion source may now be considered generally preferable to the canal ray tube.

The cathode is provided with two incandescent filaments, of which one, placed behind and perpendicular to the other, is intended for the exhaustion of the ion source, whereby the life of the second filament is appreciably increased (c. 100 hours). Each filament consists of a 10 cm length of 0.45 mm tungsten wire which is heated by a current of 15 amp. with a potential drop of about 7 volts over the wire. It is mounted on three molybdenum rods, 2 mm in diameter, fused into pyrex glass.

[1] Figures in square brackets refer to Fig. 1.

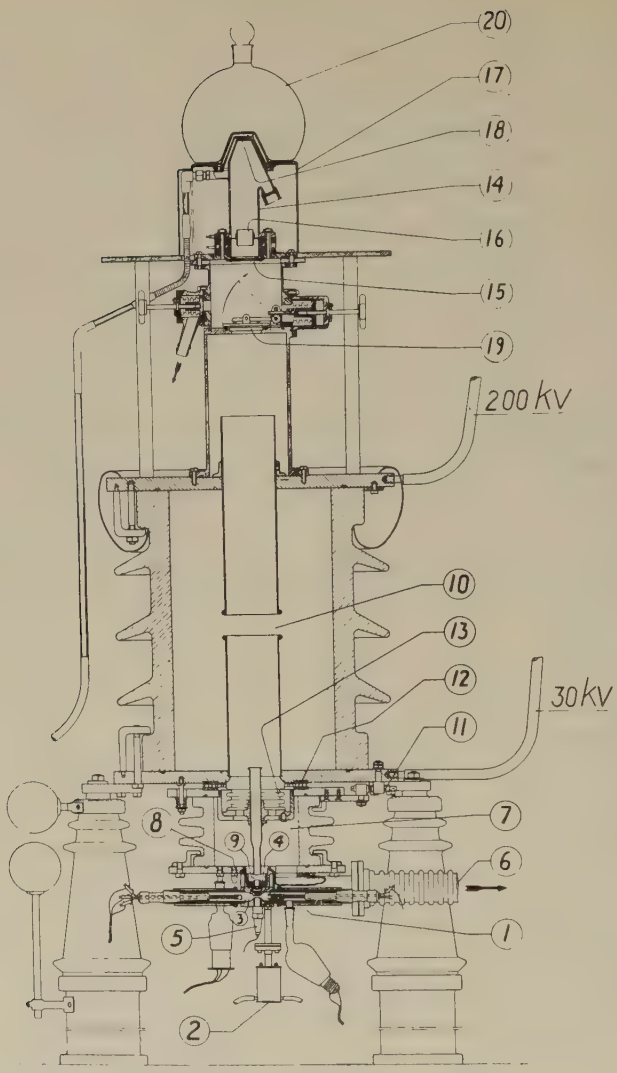

Fig. 1. Cross section of the neutron generator.

Deuterium is led to the ion source through four palladium tubes, surrounded by electrically heated metal spirals [2]. This system permits a simple and effective regulation of the gas supply at the instrument board. The gaseous pressure in the ion source is measured with a PIRANI gauge. The anode current is c. 1 amp. at an anode potential of 100 volts. The

probe [3], consisting of a steel cylinder with a channel 7 mm long and 1 mm in diameter, is insulated by means of a steatite insulator [4] and connected with a sparking plug [5] for the application of the potential. For the arc current mentioned, an optimum ionic current is obtained at a target potential of 6 kV.

The pump system (v. Fig. 2) consists of two three-inch oil diffusion pumps coupled in parallel and in series with a molecular pump and an eccentric pump. The pump intake [6] is connected to the separate chamber [7] into which the channel from the ion source opens; this gives an especially efficient pumping out of the inward leaking deuterium gas. At a pressure in the ion source of c. 0.1 mm the pressure in the high-vacuum chamber can be maintained at $2 \cdot 10^{-4}$ mm. This latter is read with a modified KNUDSEN manometer, as designed by DUMOND and PICKELS (4), coupled at [8]. This has proved to be quite well adapted to the purpose and is not damaged by a bad vacuum, which is the case for an ionisation manometer with filament, which has also been employed. Since the KNUDSEN instrument is a molecular manometer, the deflection is independent of the nature of the gas mixture. All vacuum connections consist of rubber packings and greased conical ground joints.

At a maximum potential of 200 kV a two-stage acceleration of the ions suffices. The dimensions of the electrostatic lenses have been calculated from the following empirical formula (5):

$$f = \frac{2.8\,R}{(1 + 2\,\gamma^4)\,\gamma^2}; \quad \gamma = \frac{v_1 - v_2}{v_1 + v_2} \tag{3}$$

where

f = focal length of lens

R = radius of cylinder

v_1 and v_2 = potentials of cylinders.

The first acceleration lens [9] is of 1.4 cm and the second [10] of 10 cm diameter. The distances between the cylinders may be varied, but are not critical, being about 0.7 cm and 5 cm respectively. A focussed ray is obtained in accordance with calculation at a probe potential of 6 kV, a potential of

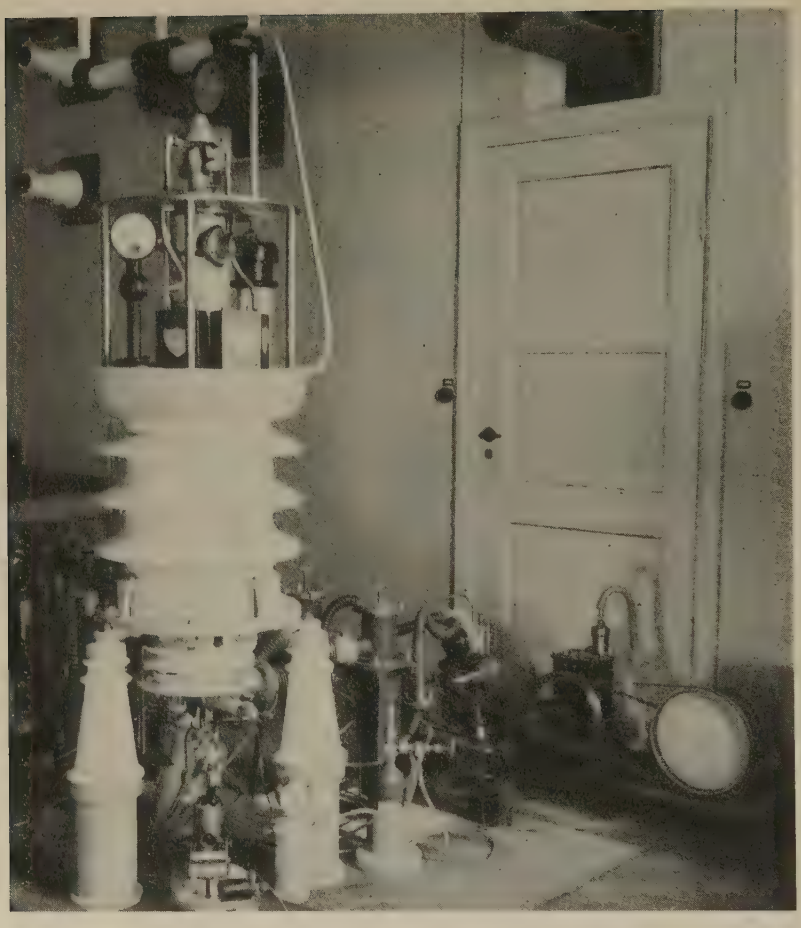

Fig. 2. Total view of the neutron generator.

40 kV on the first acceleration tube and a maximum potential of 200 kV. These potentials are provided by rectifier aggregates which were at hand in the Institute, stabilized by leak resistances to earth. The high potentials are measured with a Starke-Schröder voltmeter and an electrostatic voltmeter coupled with a high-resistance potentiometer.

The first lens has a high focussing power with a focal length of about 2 cm; the other is weak, its focal length being about 20 cm.

The ionic beam can be directed, since the whole lower part

of the apparatus supporting the ion source and the first acceleration tube can be displaced horizontally by means of the set-screws [11] the ball bearing [12] and the sylphon tube [13]. The centering of the beam is regulated by observation of the focus through a window and in a mirror arrangement at the target (v. Fig. 2).

The ionic current is measured with a microammeter. For this purpose the upper part of the apparatus [14], insulated by perspex plates, serves as a FARADAY cage. The ionic beam is limited by the shutter [15] and secondary electrons expelled at the target and at the edges of the shutter are decelerated by the insulated, movable cylinder [16] which is mounted in the shadow of the shutter and has a negative potential with respect to this and the FARADAY cage. Thanks to this arrangement, and because of the fact that the FARADAY cage is situated so far from the acceleration lens that the field from this may be neglected, it may be assumed that the effect of secondary electrons has been almost completely eliminated. The poor agreement observed by some authors between ionic currents determined directly in this manner and those determined indirectly by calorimetric measurements, may be ascribed, in the opinion of the present author, to a deficient system for the screening off of secondary electrons. In order to prevent corona currents the FARADAY cage is completely enclosed in a metal sheath [17].

Fig. 3 shows the measured current as a function of the potential on the cylinder [16]. The horizontal sections of the curve represent the cases where no, and all, secondary electrons contribute to the current measured. The potential on the cylinder [16] is provided by a battery and has normally been — 135 volts with respect to the target.

In Fig. 4 the focussing properties of the lenses are shown. At a constant probe potential of 6 kV and taking the potential of the first acceleration tube as parameter the measured ionic current has been plotted as a fuction of the maximum potential. The occurrence of a focus is denoted by a + sign. For a focussed beam the focus is about 2 mm in diameter. For continuous irradiation a broder focus is required. This is attained without an appreciable diminution of the current by

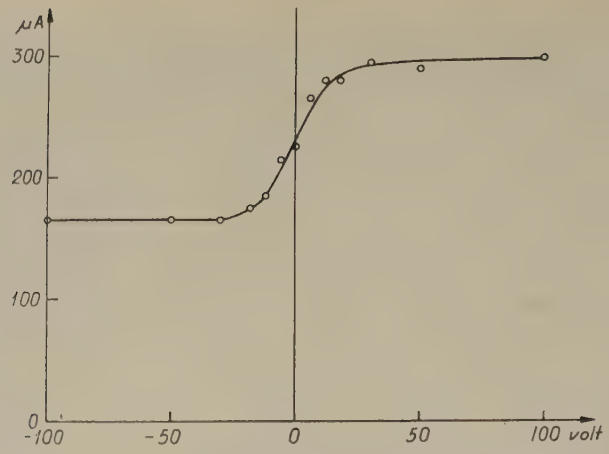

Fig. 3. Ion current as function of screening potential showing the effect of secondary electrons.

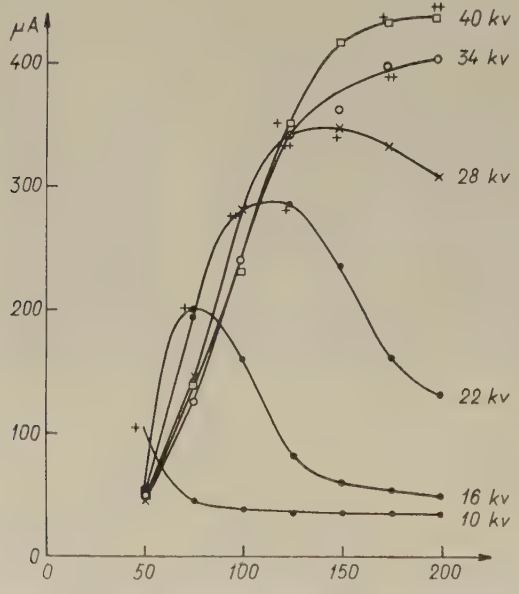

Fig. 4. Ion current as function of lens potentials.

reducing the potential on the first acceleration tube. As a rule the latter has been 30 kV for a maximum potential of 200 kV. The focus then covers the greater part of the copper plate on the target.

The target is cooled with light oil which circulates through a cooling element through which, in turn, tap water is passed. The oil is pressed between concentric cones and forced over the copper plate [18]. The thickness of the oil layer here is only 0.2 mm and thus at an oil pressure of about 1 kg. the current is rapid. The oil is circulated by means of a gear-wheeled pump. When heavy paraffin ($C_n\ D_{2n+2}$, m. p. 76°) is employed as target material, this method gives adequate cooling; in a preparative neutron generator it is decidedly preferable, for example, to cooling with liquid air.

When the paraffin is placed on the target, the upper section [14] is removed. A sealing device [19] prevents the penetration of air into the remainder of the apparatus during this procedure. The paraffin is distilled in vacuo from a small heating plate to the copper plate which is cooled with carbon dioxide snow. In this manner an extremely thin layer is obtained which conducts heat sufficiently well to prevent melting and evaporation of the paraffin during the irradiation.

A direct registration of the neutron radiation, for example with a boron trifluoride ionisation chamber, is difficult to carry out, since the neutrons are generated on the high-tension side. On the other hand integrating methods may be used without difficulty, for example the activation of Ag indicator in paraffin according to Fermi, or the method of Zimmer (6) employing a condenser ionisation chamber which was formerly introduced by Sievert (7) for measurements of X-ray doses.

If rapid neutrons pass through a hydrogen-containing material A in which there is a small air-filled space, then according to Zimmer the following relationship holds between the neutron number Z_N and the ionisation measured in the air space J_L

$$Z_N = \frac{J_L \cdot 4\pi r^2 \cdot W \cdot M_L \cdot B_A}{\alpha \cdot E \cdot \delta_A \cdot L \cdot \sigma \cdot M_A \cdot D_L \cdot B_L}. \tag{4}$$

Z_N = number of neutrons emitted from source per second.
J_L = number of ion pairs formed in air space per unit time and volume.
r = distance from volume element under consideration to neutron source.

W = work of ionisation of air ($= 32.5$ eV).
E = mean energy of neutrons ($= 2.3 \cdot 10^6$ eV).
α = mean fraction of E transferred to a proton $\left(= 1 - \frac{1}{e}\right)$
δ_A = hydrogen content of material in weight per cent $\times 10^{-2}$ ($= 0.044$).
L = Avogadro's number ($= 6.06 \cdot 10^{23}$).
σ = effective cross-sectional area of protons for neutrons of energy E ($= 1.7 \cdot 10^{-24}$ cm^2).
M_L = mean molecular weight of air ($= 29$).
M_A = mean molecular weight of material A ($= 100.4$).
$\frac{B_A}{B_L}$ = ratio between molecular stopping powers ($= 4.1$).
D_L = density of air ($= 1.29 \cdot 10^{-3}$ g/cm^3).

In the measurements bulb condenser ionisation chambers of aerion[1] have been employed. The charges have been determined with a string Edelmann-electrometer, modified for this purpose.

Under normal working conditions a neutron intensity of c. $8 \cdot 10^7$ neutrons per second is obtained, which corresponds to c. 3.5 g. Rn + Be.

The neutron generator has been in continuous service for more than a year in the preparation of radio-phosphorus from CS_2 according to the reaction:

$$^{32}_{16}\mathrm{S} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{32}_{15}\mathrm{P} + {}^{1}_{1}\mathrm{p} \qquad (5)$$

requiring fast neutrons.

Halogens, especially bromine, have also been prepared according to the general reaction.

$$^{A}_{Z}\mathrm{X} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{A+1}_{Z}\mathrm{X} \qquad (6)$$

For reactions of this type, where the effective cross-section for the nuclear process is greatest for slow neutrons, the reaction chamber has been surrounded by a paraffin layer about 10 cm thick. The reaction chamber, which is of glass, has

[1] Obtained from *Physikalisch Technische Werkstätten*, Freiburg i Br.

been given the form shown in Fig. 1 [20] so that the neutron radiation emitted radially from the target [18] may be utilised to the utmost.

A large part of the work connected with the planning of this neutron generator has been carried out by Professor The Svedberg, who has also given the author much valuable advice in the building of the apparatus.

Dr. L. H. Gray of the Physics Department, Mount Vernon Hospital, Northwood, Middlesex, has greatly facilitated this work by kindly providing the author with detailed information concerning the neutron generator constructed in his department.

The author is greatly indebted to *AB. Hammarbylampan*, Stockholm, for carrying out the fusion of molybdenum into glass for the electrodes of the ion source.

The construction of this neutron generator has been made possible by a grant from the Rockefeller Foundation.

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On the Development and the Use of the Aryl Sulphonamide Resins, Especially of Those Built Upon p-Toluene Sulphonamide.

By Allan Dahlén.

AB Bofors, Nobelkrut.

When the manufacture of saccharin was commenced, one of the greatest difficulties was to make use of the by-product p-toluene sulphonechloride, of which quantities at least as large as those of the ortho-compound were obtained. Those who were working to find an employment for that inconvenient by-product scarcely thought that it would later prove to be a valuable raw material for the manufacture of, among other things, lacquers, floor coverings and gramophone records.

It is true that the p-toluene sulphonamide became a raw material for the production of the disinfectant chloramine. The applicability increased considerably, however, when it was found that on the basis of p-toluene sulphonamide derivatives could be produced which proved to be good plasticisers, and when it was discovered that p-toluene sulphonamide and its derivatives could be condensed with formaldehyde, thus forming synthetic resins, which were useful for many purposes.

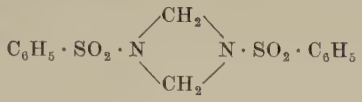
In this connection we will confine ourselves to particulars about the resins based on aryl sulphonamides.

The first mention in the literature of products obtained by condensing an aryl sulphonamide with formaldehyde seems to occur in an article by Magnus-Levy (1), who describes products formed by condensation of benzene sulphonamide with formaldehyde. He performed elementary analysis and molecular weight determinations according to Raoult and came to the conclusion that the condensation mixture consisted mainly of compounds with the general formula

$$(CH_2 \cdot N \cdot SO_2 \cdot C_6H_5)x,$$

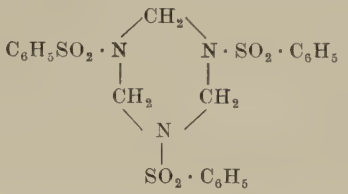
where x is equal to 2 or 3.

According to Magnus-Levy the structural formulas of these compounds should be



(1)

and



(2)

At that early stage there seemed to be no thought of practically applying the condensation products, naturally because there was no imperative need to find an outlet for the benzene sulphonamide. It was otherwise in the case of p-toluene sulphonamide.

Herzog (2) has given a summary of the work devoted to the subject up to that time. He discusses the various attempts that had been made during the years immediately preceding to employ derivatives of p-toluene sulphonechloride, such as p-toluene sulphonamide, p-toluene sulphonic acid and its esters in the production of synthetic resins. Thus he mentions that condensation products of phenols and aldehydes with non-resinous character on treatment with p-toluene sulphonechloride give hard, brittle resins with good resistance to light and air. He also speaks of resins of different hardness obtained by condensation of p-toluene sulphonamide or its alkyl derivatives with formaldehyde, these resins being colourless, neutral and soluble in different solvents. The condensation of a mixture of o- and p-toluene sulphonamides with formaldehyde is also mentioned. It is suggested that these resins would be good raw materials for the manufacture of lacquers. Furthermore, Herzog describes alkylation of natural resins by aid of the alkyl esters of p-toluene sulphonic acid, thus giving the natural resins more valuable properties for certain purposes.

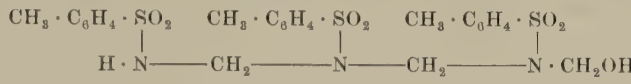
The chemical course and the result of the condensation of aryl sulphonamides and formaldehyde have been closely studied by Walter and Glück (3). These authors have shown that on condensation with formaldehyde aryl monosulphonamides form fusible resins, whereas on introduction into the aryl sulphonamide molecule of another group capable of reacting with formaldehyde, infusible and insoluble resins are generally obtained. These resins are characterized as »hardening» resins.

Walter and Glück have tried to settle the constitution of the sulphonamide-formaldehyde resins. They consider that the compounds described by Magnus-Levy only consist of decomposition products of the resins, but they are of the opinion that the molecular weights of the resins must be rather low. The authors have performed a number of experiments, but it seems that they do not wish to draw any definite conclusions as to the molecular size of the resins. Moreover, the authors have paid great attention to the products obtained by condensing formaldehyde with aryl disulphonamides and aryl trisulphonamides.

This work has been continued by Walter and Storfer (4), and Walter and Lutwak (5) have also studied the condensation of formaldehyde with benzene trisulphonamide, phenol sulphonamide and aryl sulphonanilides. Furthermore, Walter and Pollak (6) have described condensation products of aminoaryl sulphonamides and different aldehydes, such as formaldehyde, acetaldehyde and furfural. Walter and Engelberg (7) concerned themselves with products formed by condensation of naphthalene sulphonamides and formaldehyde. In a summary of his investigations Walter (8) calls attention to the difference in the properties of the resins, which depends on their formation from monosulphonamides or sulphonamides with at least two active groups. »If one active group alone is present, only one-dimensional chains or simple rings can be formed. — The capacity to 'harden' is therefore due less to a high degree of polymerisation than to the formation of ring-systems, more to the *constitution* and less to the *molecular size*».

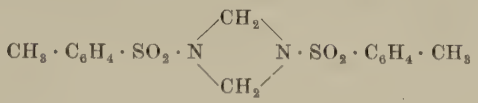
In this connection, Walter states that by treatment with

alcoholic hydrochloric acid or by heating the aryl monosulphonamides are transformed into simple compounds of the same type as was described by Magnus-Levy (1). Walter considers that the main component of a toluene sulphonamide resin is probably the methylene methylol compound



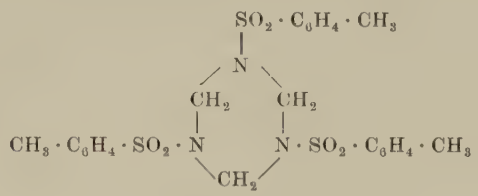
(3)

which on decomposition would give inter alia the compound



(4)

or on simple dehydration the compound



(5)

However, the relationships are probably more complicated than those sketched above. By varying the conditions at the condensation, it is possible to give a sulphonamide resin, based on two definite components, such different properties, that it must be supposed that the nature of the ingoing molecules is more fluctuating than Walter considered. On the whole, it seems that much work remains to be done in the theoretical respect, even with regard to the most simple sulphonamide resins, e. g. those based on toluene sulphonamides. It would not be presumptuous to hope that the investigations made by The Svedberg will throw light upon certain unsolved problems here, as they have done in other related spheres.

As implied above, the sulphonamide resins have also become the subject of studies in Sweden. On account of their close connection with the manufacture of saccharin, it is natural that the interest in these resins has been concentrated at *AB Bofors, Nobelkrut*, where we have gained experience as regards both the properties and the manufacture of the resins.

Our work has not yet been published, but the present author wishes to lay stress upon the researches performed by F. Friedemann and co-workers. Above all we have centred our work upon resins built up on toluene sulphonamides.

The condensation may be performed in different ways, but it seems to be the following treatment (which we call »hardening»), that is chiefly decisive of the final properties of the resins. After the condensation the water together with the main part of any formaldehyde excess is drawn of. The resin still retains certain quantities of water and formaldehyde, which must be removed. This is effected by heating the resin in the condensation vessel with or without vacuum or in thin layers on flat bowls. This treatment, however, seems to involve something more than a simple removal of the excess of water and formaldehyde. The heating to temperatures above 100° C seems to be attended by transformations in the molecules and changes of the molecular weight.

We have followed up the course of the hardening by means of the determination of the dropping point and other methods. Portions of one condensation product were treated in several different ways, whereby the temperature and the extent of the treatment were varied. The resins were poured out into flat basins with a layer thickness of 1 cm. The results of the treatment appear in Table 1.

Table 1.

Hardening of p-Toluene Sulphonamide Resins.

Temperature °C	Time (hours)	Dropping point °C
120	5	36
120	20	73
150	5	68
150	20	94

From this table it is clear how the time as well as the temperature affects the dropping point. After the hardening all resins were clear and almost colourless. The sample that had been hardened for 5 hours at 120° C was already soft at 20° C, the others, on the other hand, were brittle.

After hardening of the p-toluene sulphonamide resins for a long period, it has been found that crystals separate in the resin on cooling. This seems to be a sign of gradual alterations in the structure of the resin. Similar observations are made when the resin is heated at higher temperatures. A distinct odour of formaldehyde at high temperatures is a sign that the resin is being decomposed.

So far we have principally considered the theoretical aspect of the sulphonamide resins. As mentioned above, these resins have been practically employed during the last decades, and different types have been sought after which would be suitable for different purposes. A great number of such types have been prepared. In this connection it is our intention to treat only the toluene sulphonamide resins; other types will be mentioned only if it is necessary for the continuity of the account.

The first patents in this sphere seem to date from the year 1919 and belong to *Farbwerke vorm. Meister Lucius & Brüning in Höchst a. M.* (9). They concern processes for preparing resinous products from aryl sulphonamides or their mono-alkyl substitution products and formaldehyde, and some modes of employment for the resins are stated.

A great number of patents of the years 1929 and 1930 belong to *British Celanese Limited* (10). In the first it is pointed out that lacquers and varnishes, having an organic derivative of cellulose as their chief constituent, do not always adhere readily to a smooth surface or may become cloudy and inhomogeneous on drying. Ingredients such as resins and similar substances have therefore been sought, which, when incorporated in the composition, do not produce these disadvantages. Such a resin should be compatible with the cellulose derivative both in solution and in the dry film and should also be compatible with other ingredients of the composition. The resin must be cheap, free from watersoluble constituents and practically neutral. According to the same patent, resins prepared from benzene sulphonamide and aldehydes have proved to possess these properties. The patent describes the preparation of such resins and their use together with different cellulose derivatives, such as nitrocellulose, cellulose acetate, methyl

cellulose and ethyl cellulose. Examples of compositions for lacquers are given, and possible plasticizers are also mentioned.

Other patents belonging to the same firm treat in the same way the preparation and the employment of xylene- and toluene-sulphonamide resins. Methods are described by which the properties of for example the toluene sulphonamide resins might be varied in different ways, their applicability thereby increased. Thus the condensation of toluene sulphonamide with formaldehyde in the presence of urea is mentioned.

Further patents treat resins, built on aryl sulphonamides, which have been condensed with furfural, benzaldehyde or acetaldehyde. Among various sulphonamides, which, according to the patents could be made the bases of similar resins, the monosulphonamides of naphthalene, phenol, cresol and naphthol are mentioned.

A patent granted to Walter (11) concerns the preparation of hardening resins, built on formaldehyde and aromatic sulphonamides, which besides the sulphonamide group also contain at least one substituted or unsubstituted NH_2-group. Several examples are mentioned, where the starting materials consist of p-sulphoneamidobenzamide, m-benzene disulphonamide, xylene disulphonamides, aniline trisulphonamide, benzene trisulphonamide, phenol disulphonamide and several others.

Several sulphonamides and their employment are treated in patents granted to, among others, *Henry A. Gardner*, *Du Pont Viscoloid Company*, *Monsanto Chemical Works*, *Fahlberg-List A. G. and I. G. Farbenindustrie A. G.* (12).

The experience gained in experimental work with the sulphonamide resins has been followed by industrial manufacture of different types of these resins (13 and 14). Such manufacture seems to have been first realized in U. S. A. (15 and 16). *The Monsanto Chemical Works* have placed the resins on the market under the name of Santolites, which seem to differ from each other mainly in the different sulphonamides on which they are built up. Among the different types of resins Santolite MS, Santolite MHP, and Santolite K may be mentioned. The manufacturer recommends that they be used together with cellulose acetate or nitrocellulose.

In Germany a sulphonamide resin, called FLS-resin, is produced by *Fahlberg-List A. G.*

As mentioned above, we have carried out during recent years at *AB Bofors, Nobelkrut*, some investigations concerning the production and the properties of sulphonamide resins. We have concentrated our work on the toluene sulphonamide resins. In another connection I have already alluded to some details of the manufacture. On treating p-toluene sulphonechloride with ammonia p-toluene sulphonamide is obtained. On condensing formaldehyde with the technical variety of p-toluene sulphonamide a resin is obtained which is named *Bonoharts PS 1.* This resin is slightly coloured, owing to the use of insufficiently purified raw materials. In order to satisfy the most rigorous demands, we have elaborated an effective method of refining the sulphonamide. In the subsequent condensation it gives an almost colourless resin, named *Bonoharts PS 2.* For simple purposes we produce a resin, *Bonoharts BS*, based on a mixture of p- and o-toluene sulphonamides, which is darker and not quite clear, but its other properties are similar to those of the other Bono-resins. Generally, when the colour and the transparency are of no account, this resin, which is cheaper, can be used.

Characteristic data for these resins are obtained by determination of their softening point (melting point), dropping point and solubility in various solvents. We have found, however, that the properties of resins, built up on the same components, could be varied within certain limits, which depend on the mode of condensation and hardening (see Table 1). The softening point of the Bono resins is usually about 30° C and the dropping point about 70° C. By special treatment of the resins, these figures may be raised considerably.

The resins are readily soluble in a great number of common solvents, such as fatty acid esters, glycol, glycerine, acetone, fatty acids, diethyl carbonate, phthalic acid esters and others, The solubility in alcohols and aromatic hydrocarbons depends on the mode of manufacture of the resins, but in many cases this solubility is very good. Ethyl ether and carbon tetrachloride are bad solvents. In aliphatic hydrocarbons, drying oils and turpentine the resins are insoluble.

The resins are resistant to common sunlight as well as ultra-violet light, to a degree as excellent as could be desired of almost any resin. On the whole, the stability of the resins towards external influences must be considered satisfactory.

The employment of the sulphonamide resins has, as may be evident from the above, been made the subject of investigations at several institutions. For certain reasons we have confined ourselves to the examination of their usefulness with or without combination with nitrocellulose. In this we have had excellent collaboration with the leading enterprises in the paint and varnish industry in our country.

After melting and heating to 100—150° C, the resins are sufficiently fluid to be directly applied to a surface. The film obtained is rather brittle at 20° C, but softens on slight heating. On the addition of plasticisers such as phthalic acid esters, the films become less brittle. A resin with a high softening point ought to be chosen in order that the plasticiser may not make the resin too soft or even sticky.

The same result will be obtained, if the resin is dissolved in a suitable solvent. In this case the film desired can be made considerably thinner. The capacity of the resins to emit the solvent is rather good. Their potentialities, however, vary very much with the method of employment.

The Bono resins are very compatible with nitrocellulose and the experiments performed have proved that the resins are suitable for nitrocellulose laequers. When a film, consisting only of a resin, is too brittle, or after addition of plasticisers too soft, an addition of nitrocellulose has proved capable of giving the film the desired properties. Thus, an addition of nitrocellulose will make the resin less brittle and firmer at lower temperatures. In such a case a large amount of the plasticiser is unnecessary and the stickiness is avoided.

To sum up, it may be said that we have found that solutions of the Bono resins, with or without an addition of nitrocellulose or plasticisers, can be used to cover a surface with thin, waterstable and light-fast films. In this sphere further progress may be expected in connection with the examination of further types of resins.

The properties of the Bono resins seem to agree with those of the corresponding foreign synthetic resins (Santolites and FLS-resin). Thus it is obvious that in other countries the sulphonamide resins are used in nitrocellulose lacquers (13 and 17).

We will devote some moments to other possibilities of employing the resins which have been taken into consideration abroad. Many sulphonamide resins, on account of the differences in their properties, are suitable for different purposes. In this connection it is out of the question to give any individual descriptions. I therefore propose to treat all sulphonamide resins as a unit.

The use of the resins in nitrocellulose lacquers has already been discussed. It may be mentioned that in nitrocellulose lacquers an addition of sulphonamide resins has been made in order to produce effects arising from the formation of crystalline substances in the lacquer film. These are brought about by choosing a solvent in which the resin is insoluble or only partly soluble.

Because they are light-stable, the sulphonamide resins together with nitrocellulose, butyl acetate and toluene are used in the manufacture of laminated glass.

The sulfonamide resins have probably found their most extensive employment in association with cellulose acetate. This is very valuable, as suitable plasticisers for the cellulose acetate have hitherto been sought for. Here the resins act, in reality, as plasticisers. The nitrocellulose plasticisers camphor, phthalates and other substances are not compatible with cellulose acetate.

This was probably the reason why experiments were made with the sulphonamides themselves or certain of their derivatives as plasticisers. The first mention in the literature of sulphonamide derivatives being used as plasticisers occurs in a patent granted to William A. Lindsay (18). Since that time the use of many such derivatives as plasticisers has been described. At *AB Bofors* we have also made investigations regarding the application of such compounds as plasticisers, especially in association with nitrocellulose. Certain quantities are now sold for such purposes in this country.

On the other hand, we have as yet had no reason to be interested in the employment of the products concerned in association with cellulose acetate. A comprehensive examination of the problems concerned has been made by Carswell (19). He describes the properties of benzene sulphonamide, toluene sulphonamide, xylene sulphonamide, their methyl and ethyl derivatives, p-toluene sulphonanilide and finally p-toluene methylene sulphonamide. However, the last-mentioned compound is not quite comparable with the others, since p-toluene methylene sulphonamide is known chiefly in its polymerised form as a type of sulphonamide resin. This is also observed by Carswell. He has also found that p-toluene sulphonamide shows a much greater affinity for cellulose acetate than the other sulphonamide derivatives.

The other sulphonamide resins which appear to be used in association with cellulose acetate are, for example, those built on anisole sulphonamide.

The sulphonamide resins could advantageously be combined with ethyl cellulose, benzyl cellulose and cellulose octobutyrate. Thus they increase the flexibility of ethyl cellulose films.

It is very significant that the sulphonamide resins are compatible with polyvinyl acetate resins, increasing the flow at elevated temperatures and improving the workability. In this combination a plasticiser of the sulphonamide type may suitably be added. The use of volatile solvents may thereby be avoided, and the mixtures are obtained by simply heating and mixing the components.

The sulphonamide resins are soluble in alkaline solutions, where they are slowly decomposed. Such solutions are used for covering viscose threads and viscose films with waterproof coatings. At the same time the electrical resistance is improved. When artificial silk is treated with sulphonamide resins, it acquires an appearance more suggestive of that of natural silk.

Use has been made of the sulphonamide resins even in the manufacture of certain objects, such as artificial brushes. In such cases, however, quite special types of resins are concerned. Nowadays gramophone records are manufactured where sulphonamide resins enter as components.

From what has been said above, it is evident that wide possibilities exist for the use of the sulphonamide resins. Much still remains to be done. In order to increase their applicability, condensation with other resin components, such as phenols, urea and several others seems to offer promise.

We have also examined the possibilities, already mentioned, of effecting the condensation of sulphonamides with other aldehydes, above all furfural. The resins obtained in this manner are generally darker than those built on formaldehyde. They will nevertheless probably be used for certain purposes, especially if, from the maintenance point of view, there prove to be advantages in building on furfural instead of formaldehyde.

We ought to foster the resources existing within our country to provide ourselves with important raw materials. We hope therefore, that the work now progressing with the end of developing the sulphonamide resins and making them still more useful, will be crowned with success.

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Über α,β-Dialkyl-stilbenchinone, neue synthetische Östrogene.[1]

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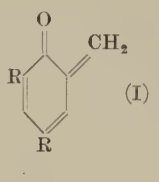
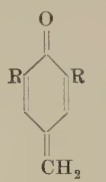
Im Verlaufe von Untersuchungen über die Reaktionen, die sich bei der Ausbildung von Makromolekülen auf Phenol-Formaldehydbasis, insbesondere bei der thermischen „Härtung" der Resole, abspielen, hatten wir gefunden, dass Phenolalkohole beim trockenen Erhitzen neben anderen Verbindungen auch Chinonmethide (Methylenchinone, I, II) liefern (1).



(I)



(II)

Diese schon von Zincke (2), v. Auwers (3), Fries (4) und Pummerer (5) studierten Körper sind in monomerer Form nicht stabil, sondern gehen alsbald nach ihrer Entstehung Di- und Trimerisierungen ein. Wir waren auf Grund unserer Versuche zu dem Schluss gekommen, dass solche Di- und Trimerisierungen von endständigen Chinonmethidgruppen in den „härtenden" Resolmolekülen wesentlich zur Ausbildung der fertigen Riesenmoleküle, der Resite, beitragen dürften. Zur gleichen Auffassung war etwa gleichzeitig auch Hultzsch (6) gelangt.

Die Chemie der Chinonmethide, insbesondere das Wesen ihrer Stabilisierungsreaktionen, also jener Di- und Trimerisierungen, welche die monomeren Chinonmethide vom Typus

[1] Zugleich III. Mitteilung in der Untersuchungsreihe „Studien über Chinonmethide" (II. Mitt. s. (8)).

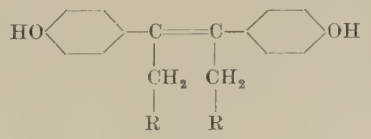
(I) und (II) eingehen, ist noch verhältnismässig wenig untersucht. Schon die ältere Literatur weist jedoch auf eine Vielfalt von Reaktionsmöglichkeiten, und unsere eigenen Versuche (7, 8) haben gezeigt, dass man je nach der Art der Kernsubstituenten verschiedene derartige Stabilisierungsreaktionen erhält.

In Fortsetzung unserer Studien über diese ausserordentlich reaktionsfähige Substanzgruppe haben wir auch die Untersuchung solcher Chinonmethide in Angriff genommen, die an der Methylengruppe substituiert sind, einesteils, weil hierdurch Chinonmethide mit erhöhter Beständigkeit zu erwarten waren, andernteils, weil es von Interesse schien, zu erfahren, ob bei alkylsubstituierten Chinonmethiden vom Typus der Formel (III)

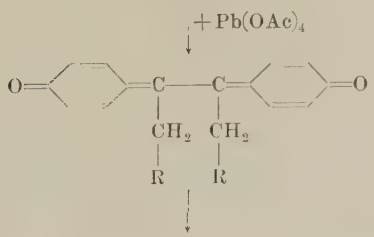
(III) (IV)

anstelle der Dimerisierung eine intramolekulare Stabilisierung durch H-Verschiebung eintreten würde. Eine solche sollte bei einem methylsubstituierten Chinonmethid ((III), R=H) zu dem bisher unbekannten p-Vinylphenol ((IV), R=H) führen. Über diese Versuche hoffen wir bald berichten zu können.

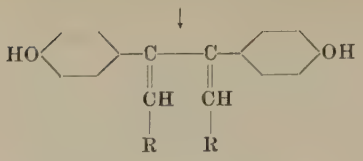
In der vorliegenden Mitteilung beschreiben wir eine eigentümliche *Stabilisierungsreaktion*, die von den *α,β-Dialkyl-stilbenchinonen* (VII, VIII) gegeben wird. Wie ein Vergleich der Formeln (VII) und (VIII) mit Formel (III) zeigt, stehen diese Dialkylstilbenchinone formell in naher Beziehung zu den an der Methylengruppe substituierten Chinonmethiden.



R=H (V)
R=CH_3 (VI)



R=H (VII)
R=CH_3 (VIII)



R=H (IX)
R=CH_3 (X)

α,β-Dialkyl-stilbenchinone sind bisher nicht bekannt gewesen. An der Äthylenbrücke unsubstituierte Stilbenchinone sind dagegen schon von Zincke (9), Goldschmidt (10) und Fries (11) gewonnen und ziemlich eingehend untersucht worden. Zincke hat bereits darauf hingewiesen, dass man die Stilbenchinone als „doppelte Chinonmethide" betrachten könne, und tatsächlich spiegelt sich in der Neigung dieser Substanzen, Stoffe wie HBr, HOAc, AcOAc an den äussersten Enden des chinoiden Systems, d. h. am Sauerstoff und an der Methingruppe, anzulagern, das Verhalten der Chinonmethide wieder.

Die nun von uns erhaltenen α,β-Dialkyl-stilbenchinone (VII, VIII) wären dementsprechend als „doppelte substituierte Chinonmethide" aufzufassen und man könnte erwarten, dass sie sich in ihrem Verhalten den Verbindungen vom Typus (III) nähern würden.

Die Gewinnung der Dialkyl-stilbenchinone gelang durch *Dehydrierung der* zugrundeliegenden *4,4'-Dioxy-α,β-dialkyl-stilbene* (V) *und* (VI) *mittels Bleitetraacetat.* Die genannten Stilbene sind von Dodds und Mitarbeitern (12) zum ersten Mal dargestellt worden. Sie sind bekanntlich durch hohe östrogene Wirksamkeit ausgezeichnet; die Diäthylverbindung ((VI), „Diäthylstilböstrol") ist etwa ebenso wirksam wie natürliches weibliches Sexualhormon (Östron).

Beide Dioxystilbene reagieren, in Benzol, Äthylacetat, Chloroform oder Äther gelöst, augenblicklich mit Bleitetraacetat; unter raschem Durchschreiten einer blaugrünen Chinhydronstufe färbt sich die Lösung rotgelb. Zur vollständigen Dehydrierung wurde 1 Mol. $Pb(OAc)_4$ pro Mol. Stilben verbraucht, wobei entsprechend der Gleichung

$$\text{Dioxystilben} + Pb(OAc)_4 = \text{Stilbenchinon} + Pb(OAc)_2 + 2\,AcOH$$

1 Mol. $Pb(OAc)_2$ ausfiel.

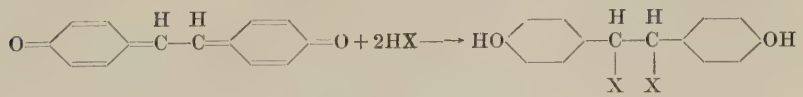
Die Stilbenchinone (VII) und (VIII) hinterbleiben beim vorsichtigen Eindampfen ihrer von der gebildeten Essigsäure durch

Ausschütteln mit Bicarbonat befreiten Lösung als rote Lacke, die leicht löslich sind in Äther, Alkohol, Äthylacetat, schwerer in Chloroform und Benzol, aus denen sie beim Abkühlen als rote Öle ausfallen; sie sind schwerlöslich in Hexan. Sie konnten bisher nicht kristallisiert erhalten werden, im Gegensatz zu den oben erwähnten an der Äthylenbrücke nicht substituierten Stilbenchinonen, die schwerlösliche, wohlkristallisierte Körper darstellen. Da die Dialkylstilbenchinone gegen Erwärmen empfindlich sind und bei Umlösungsversuchen nur sehr schwer von beigemengtem Lösungsmittel befreit werden konnten, war es bisher nicht möglich gewesen, sie zur Analyse zu bringen.

Dass den Dehydrierungsprodukten der Stilbene (V) und (VI) die Stilbenchinonformeln (VII) und (VIII) zukommen, unterliegt jedoch keinem Zweifel. Ausser ihrer Bildungsweise und ihrer Farbe spricht hierfür auch der Umstand, dass sie bei der *katalytischen Hydrierung* (mit Pt aus PtO_2 in Äthylacetat) rasch 1 Mol. H_2 aufnehmen, wobei wieder die zugrundeliegenden *Dioxystilbene* erhalten werden. In derselben Weise hatten wir früher (13) die Hydrierung des 3,5,3′,5′-Tetramethyl-stilbenchinons zum entsprechenden Dioxystilben vollzogen.

Vom äthylsubstituierten Stilben (VI) sind sowohl die trans-Form, das „Diäthylstilböstrol", wie die — biologisch viel weniger aktive — cis-Form bekannt (14). Bei der eben erwähnten katalytischen Hydrierung des Stilbenchinons (VIII) entstand in weitaus überwiegender Menge Diäthylstilböstrol (Schmp. 173°). Als Nebenprodukt wurde auch das cis-Stilben (Schmp. 149—151°) beobachtet.

Die an der Äthylenbrücke nicht substituierten Stilbenchinone reagieren nach Zincke, wie oben bereits erwähnt, beim Erhitzen mit HBr bzw. CH_3COOH unter Anlagerung in folgender Weise:

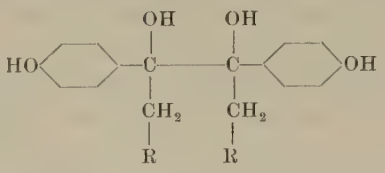


(X = Br bzw. $OCOCH_3$)

Beim Versuch, Essigsäure an die α,β-Dialkyl-stilbenchinone anzulagern, trat nun überraschenderweise eine derartige Reaktion nicht ein. Vielmehr erfolgte bereits in der Kälte sehr

rasch eine *Umlagerung* der Chinone in kristallisierte, farblose Substanzen von *phenolischem* Charakter.

Aus dem *α,β-Dimethyl-stilbenchinon* (VII) entstand so in guter Ausbeute das *2,3-Di-(p-oxyphenyl-)butadien(-1,3)* (IX) vom Schmp. 166—167°. Dieses Dien ist bereits von Dodds und Mitarbeitern (12) durch Abspaltung von 2 Mol. H_2O aus dem Pinakon (XI)

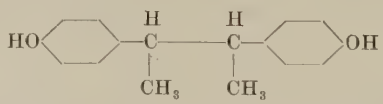


R=H (XI)

R=CH₃ (XII)

erhalten worden. Die Angaben der genannten Autoren bezüglich des Schmelzpunktes (164—165°) und der Kristallform der Substanz stimmen mit unseren Befunden überein, und die Elementaranalyse lieferte die für das Dien geforderten Werte. Die Substanz gab ein *Diacetat* vom Schmp. 129—130°. Dodds und Mitarb. geben den Schmelzpunkt dieses Diacetats zu 118—119° an. Wir stellten nun das Butadien-diacetat auch aus Pinakon (XI) nach Dodds (12) dar und fanden, dass es den gleichen Schmelzpunkt wie unser Diacetat besitzt. Der Mischschmelzpunkt zwischen beiden Präparaten zeigte keine Depression. Die Schmelzpunktsangabe von Dodds (12) dürfte daher auf einem Irrtum beruhen. Die Verseifung des nach Dodds dargestellten Diacetats lieferte das Butadien (Schmp. 166—167°), das sich durch Mischschmelzpunkt ebenfalls als identisch mit unserem Umlagerungsprodukt (IX) erwies.

Bei der *katalytischen Hydrierung*, z. B. mit Pd in Alkohol, nahm das Butadien (IX) *2 Mol.* H_2 auf und ging in das kürzlich von Adler, Euler und Gie (15) auf anderem Wege erhaltene *meso-2,3-Di-(p-oxyphenyl-)butan* (XIII) vom Schmp. 231—232° („Butöstrol") über.



(XIII)

Das vom Diäthylstilböstrol (VI) abgeleitete *Stilbenchinon* (VIII) verhielt sich in Gegenwart von *Eisessig* ganz analog wie das Methylhomologe (VII). Versetzte man z. B. eine Lösung des

Chinons (VIII) in Benzol mit etwas Eisessig, so trat alsbald eine Aufhellung der Lösung ein, und es kristallisierte ein farbloser, alkalilöslicher Körper aus, der bei *184—185°* schmolz und dessen Zusammensetzung auf die Formel $C_{18}H_{18}O_2$ eines *Dioxydiphenyl-hexadiens* stimmte. Er lieferte ein bei 147—148° schmelzendes *Diacetat*.

Dodds und Mitarb. (12) haben durch Dehydratisierung des Pinakons (XII) ein Dioxydiphenyl-hexadien erhalten, das jedoch bei *226—227°* schmilzt; es ist östrogen hochwirksam und wird auch als „*Dienöstrol*" bezeichnet.

Da nun aber für ein Dien der Formel (X) 3 Raumisomere möglich sind — im Gegensatz zum Dien (IX), von dem nur eine einzige Form existiert — so konnte man annehmen, dass in dem Dodds'schen und dem von uns erhaltenen Dien zwei verschiedene Raumisomere vorliegen. Während wir mit der Durchführung der hier beschriebenen Versuche beschäftigt waren, erschien eine Arbeit von Hobday und Short (16), in der über ein „*Isodienöstrol*" vom Schmp. *189°* berichtet wird. Diese Substanz wurde erhalten, wenn der Dimethyläther des bei 226—227° (bzw. 230—233° nach Hobday und Short) schmelzenden „Dienöstrols" mittels alkoholischem KOH bei 220° entmethyliert wurde. Durch Permanganatabbau und Ozonolyse konnten die Autoren zeigen, dass in dem bei 189° schmelzenden Entmethylierungsprodukt die Doppelbindungen an derselben Stelle liegen wie im Dienöstrol. Es dürfte keinem Zweifel unterliegen, dass das von uns erhaltene *Umlagerungsprodukt des Chinons* (VIII) mit dem Isodienöstrol von Hobday und Short identisch ist, d. h., dass ihm die *Formel* (X) eines *Hexadiens* zukommt.

Bei der Methylierung des Umlagerungsproduktes vom Schmp. 184—185° wurde ein öliger Dimethyläther erhalten, was in Einklang mit den Angaben von Hobday und Short steht. Die *katalytische Hydrierung*, z. B. mit Pd in Alkohol oder Eisessig oder mit PtO_2 in Äthylacetat lieferte nach Aufnahme von 2 Mol. H_2 ein Gemisch, das der Hauptmenge nach aus *meso-3,4-Di-(p-oxyphenyl-)hexan*, dem sog. „*Hexöstrol*" (12, 17, 18, 19) vom Schmelzpunkt 183° bestand (Identifizierung durch Mischschmelzpunkt mit authentischem Präparat), während in kleinerer Menge die ebenfalls bekannte *Racemform* derselben Ver-

bindung (Schmp. 128°) isoliert wurde. Hobday und Short haben dasselbe Ergebnis bei der Hydrierung ihres Isodienöstrols mittels Pd-Tierkohle erhalten.

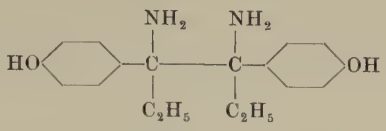
Die eigentümliche Umlagerung zu den Dienen, welche die α,β-Dialkyl-stilbenchinone, wie eben gezeigt, unter dem Einfluss von Essigsäure erleiden, bedingt, dass man bei der Darstellung der Chinone durch Dehydrierung mittels Bleitetraacetat nach beendeter Reaktion und Abfiltrieren des gebildeten Bleiacetats die nach Gleichg. S. 248 entstandene Essigsäure sorgfältig entfernen muss, wenn man das Chinon als solches isolieren will. Unterlässt man die Abtrennung der Essigsäure, so tritt nach dem Abdampfen des Lösungsmittels i. V. die Umlagerung des Chinons ein: der rotbraune ölige Rückstand kristallisiert rasch durch und man erhält durch Umkristallisieren das entsprechende Dien.

In von Essigsäure befreiten Lösungen sind die Chinone bei Zimmertemperatur stabil. Schon beim 3-stündigen Erwärmen einer Benzollösung des Chinons (VIII) auf dem Wasserbad erfolgte jedoch die Umlagerung zum Hexadien (X).

Diese Umlagerung wird ferner nicht nur durch Essigsäure, sondern auch durch *Mineralsäuren* katalysiert; z. B. wurde das Hexadien schon durch Schütteln einer ätherischen Lösung des Stilbenchinons (VIII) mit verd. H_2SO_4 gebildet.

Ebenso leicht tritt die Umlagerung unter der Einwirkung von *Alkali* ein. Unterschichtet man z. B. eine ätherische Lösung des Dimethylstilbenchinons (VII) mit verd. NaOH, so färbt sich die Lauge an der Schichtgrenze violett, und beim Durchschütteln geht die gesamte Substanz unter allmählicher Entfärbung der Ätherschicht und Verschwinden der violetten Intermediärstufe in die Lauge über. Durch Ansäuern erhält man das Dien (IX) in guter Ausbeute. Diese Reaktion verläuft ganz ähnlich auch beim Diäthyl-stilbenchinon (VIII), nur dass hierbei eine violette Zwischenstufe nicht beobachtet werden kann, vielleicht wegen der Bildung brauner alkalilöslicher Nebenprodukte. Auch beim Schütteln mit Soda- und sogar schon beim längeren Stehen mit Bikarbonatlösung lagern sich die Stilbenchinone in die Diene um. Ebenso entstand beim Versuch, gasförmiges NH_3 an das in Benzol gelöste Diäthyl-stilbenchinon anzulagern, ausschliesslich das Hexadien (X).

Der letztgenannte Versuch war in der Absicht angestellt worden, zu einer Verbindung der Formel (XIV)



(XIV)

zu gelangen, von welcher nach den Untersuchungen von Lettré (20) möglicherweise Mitosegiftwirkung zu erwarten wäre.

Die im vorangehenden beschriebene mit grosser Leichtigkeit verlaufende Stabilisierungsreaktion der α.β-Dialkylstilbenchinone besteht formell in einer intramolekularen Wanderung je eines H-Atoms aus den seitenständigen Alkylgruppen an die Chinonsauerstoffatome, eine Reaktion, die auf den ersten Blick sehr eigentümlich erscheint.

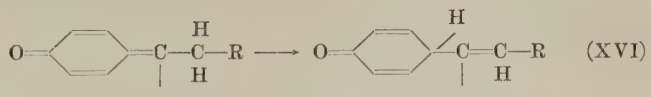
Sie kann jedoch in gewisse Analogie gesetzt werden zur Erscheinung der sog. „*Dreikohlenstofftautomerie*" (21), die ja im Endeffekt in der Verschiebung einer >C=C<-Doppelbindung unter Wanderung eines H-Atoms besteht. Hierher gehört z. B. die von Fittig (22) aufgefundene gegenseitige Überführbarkeit von α,β- in β,γ-ungesättigte Säuren in heissem Alkali, z. B.

$$CH_2{=}CH \cdot CH_2 \cdot COOH \rightleftarrows CH_3 \cdot CH{=}CH \cdot COOH$$

Das allgemeine Schema der „Dreikohlenstofftautomerie"

$$>C{=}C{-}C< \rightleftarrows >C{-}C{=}C<$$
$$\quad\ |\ H \qquad\quad H\ |$$

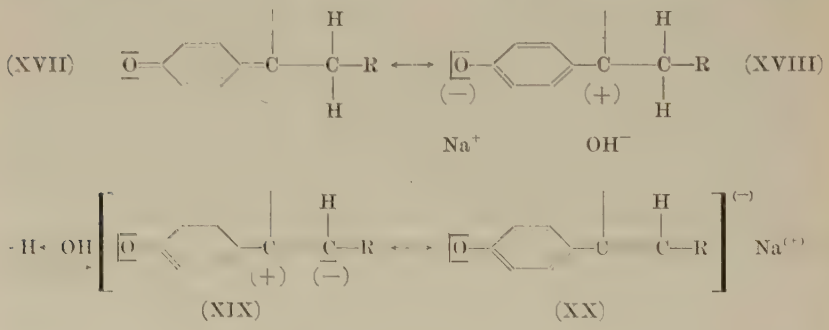
würde in der Anwendung auf unseren Fall folgende Form annehmen:

(XV)  (XVI)

Das demnach zu erwartende in (XVI) formulierte primäre Umlagerungsprodukt des Stilbenchinons (XV) wäre aber nichts anderes als eine tautomere (Keto-)Form des phenolischen Endprodukts. Während aber die typischen Umlagerungen der „Dreikohlenstofftautomerie" gewöhnlich recht drastischer Mittel bedürfen (starke H_2SO_4, heisses Alkali, Äthylat, vgl. Linstead und Noble (23)), verläuft die Umlagerung im Fall der

Stilbenchinone unter sehr milden Bedingungen. Man wird also annehmen dürfen, dass hier die Tendenz des chinoiden Systems in das energieärmere benzoide überzugehen, die treibende Kraft für die Umlagerung darstellt. Diese lässt sich dann z. B. für den Fall der Umlagerung mittels verdünnter Natronlauge vielleicht in folgender Weise anschaulich machen:

Die Stilbenchinonform (XVII) steht in Mesomeriebeziehung zu der benzoiden polaren Grenzanordnung (XVIII); diese Polarisation wird durch das NaOH begünstigt, und von hier aus erfolgt die Stabilisierung des benzoiden Systems durch Ablösung eines Protons aus der Alkylseitenkette. Hiermit wäre die eigentliche Umlagerung vollzogen, denn das entstehende Ion (XIX) ist ja bereits eine mesomere Grenzanordnung des Dien-anions (XX).



Östrogene Wirksamkeit.

Für das Verhalten der Dialkyl-stilbenchinone im Tierkörper ist die Annahme am wahrscheinlichsten, dass eine Hydrierung zu den zugrundeliegenden Stilbenen erfolgt. Natürlich ist auch eine Umlagerung zu den Dienen in Betracht zu ziehen. Für das Diäthyl-stilbenchinon (VIII) wäre also entweder die dem Diäthylstilböstrol (VI) eigene hohe östrogene Aktivität zu erwarten oder die noch nicht bekannte Aktivität des Diens (X) bzw. eine Aktivität, die zwischen diesen beiden liegt.

Wir haben Diäthylstilbenchinon (frisch dargestellt und — um Umlagerung in das Dien zu vermeiden — ohne Erwärmen in Olivenöl gelöst) im Allen-Doisy-Test an der kastrierten Ratte geprüft und gefunden, dass es in einer Menge von 10 γ noch voll wirksam ist. Weitere Prüfungen sind im Gange.

Das Hexadien (X) („Isodienöstrol") vom Schmelzpunkt 184—185°, dessen Prüfung ebenfalls noch nicht abgeschlossen ist, erwies sich als unwirksam in einer Dosis von 10 γ.

Das Dodds'sche hochschmelzende Hexadien (Schmp. 226—227°, „Dienöstrol") besitzt nach einer neuen Arbeit von Dodds (24) annähernd die gleiche Aktivität wie Diäthylstilböstrol. Somit scheint sich bei den Hexadienen die sterische Anordnung in einer ähnlichen Weise auszuwirken wie bei den Stilbenen. Bei den letzteren ist der Unterschied zwischen cis- und trans-Form gross; für das Dipropionat des ψ-Diäthylstilböstrols (=cis-Form) finden nämlich Walton und Brownlee (14) nur 1/600 der Wirksamkeit vom Dipropionat des Diäthylstilböstrols (=trans-Form). Das freie ψ-Diäthylstilböstrol soll nach den gleichen Autoren allerdings nur 14 Mal schwächer sein als das freie Diäthylstilböstrol.

Versuche.

α,β-Dialkyl-stilbenchinone (VII, VIII).

Als Beispiel für die Gewinnung der Dialkyl-stilbenchinone sei die Dehydrierung des Diäthylstilböstrols beschrieben.

3,7 g Diäthylstilböstrol wurden in einem Gemisch von 80 ml Chloroform und 40 ml Äther gelöst und in die Lösung wurden unter Turbinieren 6,2 g Bleitetraacetat[1] (entspr. 1 Mol. pro Mol. Stilben) in kleinen Portionen eingetragen. Man wartete zwischen den Zusätzen jeweils, bis die Chinhydronfarbe verschwunden war und die Lösung eine rotgelbe Farbe angenommen hatte. Nach Beendigung der Dehydrierung saugte man die Lösung, die das Diäthylstilbenchinon enthielt, von dem gebildeten Niederschlag ab. Letzterer bestand zum grössten Teil aus Bleidiacetat, das durch Auswaschen mit Wasser abgetrennt werden konnte. Hierbei erhielt man einen geringen wasserunlöslichen Rückstand (260 mg), der sich als das Bleisalz des Diäthylstilböstrols erwies; er lieferte beim Zerlegen mit heisser Essigsäure 150 mg reines Diäthylstilböstrol.

[1] Für die Darstellung eines haltbaren Präparates von Bleitetraacetat hat sich die von Mendel (25) angegebene Modifikation der Methode von Dimroth und Schweizer (26) bestens bewährt. Eine geeignete Menge des eisessigfeuchten Präparates wurde jeweils vor dem Versuch in einem Wägeglas über festem KOH i. V. zur Gewichtskonstanz getrocknet.

Die Dehydrierung kann, wie S. 248 bereits erwähnt, ebenso gut in anderen Lösungsmitteln ausgeführt werden. Man erhält jedoch eine relativ grössere Menge von nicht umgesetztem Diäthylstilböstrol-Bleisalz beim Arbeiten in Benzol und fast kein solches beim Arbeiten in Äthylacetat.

Will man das Dialkyl-stilbenchinon in unveränderter Form erhalten, so befreit man seine Lösung von der während der Dehydrierung gebildeten Essigsäure durch Ausschütteln mit konz. Bicarbonatlösung. Dann erhält man nach dem Trocknen der Lösung mit Na_2SO_4 und Eindampfen i. V. (Überhitzen vermeiden!) das Stilbenchinon als bräunlichrotes Harz von den S. 249 angegebenen Löslichkeitseigenschaften.

Die Darstellung des *Dimethyl*-stilbenchinons (VII) verläuft ganz analog wie voranstehend beschrieben.

Umlagerung der Dialkyl-stilbenchinone (VII) und (VIII) zu 2,3-Di-(p-oxyphenyl-)butadien(-1,3) (IX) bzw. 3,4-Di-(p-oxyphenyl-)hexadien(-2,4) (X).

Von den S. 250—252 bereits angegebenen Möglichkeiten zur Umlagerung der Chinone in die Diene sei nur diejenige mit Alkali näher beschrieben, und zwar für den Fall des Diäthylstilbenchinons (IX).

Die im voranstehend beschriebenen Versuch erhaltene gelbrote Chloroform-Ätherlösung des Chinons wurde mit 150 ml Äther verdünnt und mit 65 ml n NaOH geschüttelt. Die Farbe der Ätherlösung verschwand allmählich. Aus der bräunlich gefärbten Alkalischicht wurde durch Neutralisieren das Dien ausgefällt, und dieses nach einigem Stehen im Kühlschrank abgesaugt. Aus Benzol erhielt man kristallbenzolhaltige farblose lanzettförmige Blättchen oder Nadeln vom Schmp. 184—185°. Die Ausbeute betrug 73 % vom eingesetzten Diäthylstilböstrol; korrigiert man für das nicht in Reaktion getretene, als Pb-salz ausgefallene Diäthylstilböstrol (s. o.), so berechnet sich die Ausbeute an Hexadien zu 76 % vom tatsächlich umgesetzten Diäthylstilböstrol.

Das Hexadien färbt sich am Lichte bzw. beim Erwärmen leicht rötlich und wird am besten im evakuierten Gefäss dunkel aufbewahrt.

40,8 mg Subst.:	121,1 mg CO_2	24,8 mg H_2O
$C_{18}H_{18}O_2$	Ber. C 81,17	H 6,81
	Gef. C 80,97	H 6,80

Diacetat. Durch ½-stündiges Erwärmen des Hexadiens mit Pyridin-Essigsäureanhydrid auf dem Wasserbad. Aus Alkohol umkristallisiert, Prismen vom Schmp. 147—148°.

38,5 mg Subst.:	106,35 mg CO_2	21,2 mg H_2O
$C_{22}H_{22}O_4$	Ber. C 75,41	H 6,33
	Gef. C 75,37	H 6,16

Das Butadien (IX) kristallisierte aus Benzol in Nadeln oder Blättchen vom Schmp. 166—167°.

46,58 mg Subst.:	137,67 mg CO_2	24,40 mg H_2O
$C_{16}H_{14}O_2$	Ber. C 80,65	H 5,92
	Gef. C 80,65	H 5,86

Diacetat. Durch 1-stündiges Erwärmen des Butadiens X mit Pyridin-Essigsäureanhydrid wurde ein bei 119—125° schmelzendes Rohprodukt erhalten, dass nach mehrmaligem Umkristallisieren aus Alkohol bei 129—130° schmolz (Prismen). Da dieser Schmelzpunkt von dem von Dodds und Mitarb. (12) angegebenen (118—119°) abweicht, wurde die Acetylierung einmal durch 16-stündiges Stehenlassen mit Pyridin-Essigsäureanhydrid bei Zimmertemperatur, ein anderes Mal durch 15 Min. langes Kochen mit Essigsäureanhydrid wiederholt. Beide Male wurde aber dasselbe Diacetat erhalten wie im ersten Versuch.

40,35 mg Subst.:	109,90 mg CO_2	19,83 mg H_2O
$C_{20}H_{18}O_4$	Ber. C 74,52	H 5,63
	Gef. C 74,33	H 5,50

Bei der Verseifung des Diacetats mittels alkoholischer Kalilauge wurde das Butadien (X) vom Schmelzpunkt 167° zurückerhalten; der Mischschmelzpunkt zeigte keine Depression.

Katalytische Hydrierung des Diäthyl-stilbenchinons (VIII).

500 mg Diäthylstilböstrol, gelöst in 25 ml trockenem Äthylacetat wurden durch allmähliches Zugeben von 828 mg Bleitetraacetat dehydriert. Der entstandene Niederschlag bestand

aus 560 mg (ber. 606 mg) Bleiacetat und 11 mg PbO_2; Diäthylstilböstrol-Bleisalz war nicht gebildet worden. Die vom Niederschlag befreite gelbrote Lösung des Chinons wurde mit Bicarbonat behandelt, und mit Pt aus 50 mg PtO_2 unter H_2 geschüttelt. Bereits nach 15 Min. war die theoretische Menge (1 Mol) H_2 verbraucht und die Lösung nahezu farblos. Der Abdampfrückstand lieferte beim Umkristallisieren in guter Ausbeute die typischen langen Kristallbenzol-haltigen Nadeln des Diäthylstilböstrols, die beim Trocknen auf dem Wasserbad verwitterten und dann bei 171° schmolzen. Der Mischschmelzpunkt gab keine Depression.

Eine wie voranstehend bereitete Lösung des *Dimethyl*-stilbenchinons verhielt sich bei der Hydrierung unter denselben Bedingungen weniger einfach. Die H_2-Aufnahme setzte nach Verbrauch von 1 Mol H_2 mit verminderter Geschwindigkeit fort, und die Aufarbeitung eines Hydrierungsversuches, welcher nach dem Verbrauch der für 1 Mol berechneten Menge H_2 unterbrochen wurde, ergab ein Gemisch von Dimethylstilböstrol und vermutlich „Butöstrol".

Katalytische Hydrierung des Hexadiens (X).

266 mg Hexadien (X) (Schmp. 184—185°) wurden, in 30 ml Eisessig gelöst, mit 50 mg Pd-Mohr in H_2-Atmosphäre geschüttelt. Nach ca. 11 Stdn. waren 2 Mol H_2 verbraucht worden. Aus der stark eingeengten Lösung kristallisierte Hexöstrol vom Schmp. und Mischschmelzpunkt 180—183° in einer Ausbeute von 50 % der Theorie. Aus der vom Eisessig befreiten Mutterlauge wurde durch Umkristallisieren eine kleine Menge racem-3,4-Di-(p-oxyphenyl-)n-hexan isoliert, das durch Schmelzpunkt und Mischschmelzpunkt mit einem durch katalytische Hydrierung von Diäthylstilböstrol (18, 19) erhaltenen Präparat identifiziert wurde.

Katalytische Hydrierung des Butadiens (IX).

200 mg Butadien (9), in 40 ml Alkohol gelöst, wurden mit 60 mg Pd-Mohr hydriert. Der Abdampfrückstand schmolz nach dem Umkristallisieren aus Eisessig (Prismen) bei 226°

und gab mit meso-2,3-Di-(p-oxyphenyl-)butan vom Schmp. 230° keine Depression.

Adler, Euler und Gie (15) hatten diesen Körper vor kurzem bei der Einwirkung von HJ—P auf das Pinakon (XI) erhalten und wegen seiner hohen östrogenen Wirksamkeit als Butöstrol bezeichnet. Durch die eben beschriebene Bildung aus dem Butadien (IX) ist seine Konstitution nun gesichert.

Frl. Ing. Marianne Lundin und Frl. Ing. Elsa Ericsson danken wir auch hier bestens für wertvolle Hilfe.

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On the Use of Melting Point Curves for the Establishment of Steric Relationships Between Optically Active Compounds.

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Nearly fifty years have passed since the Walden inversion was discovered (1) and it was realised that a substitution at an asymmetrical carbon atom sometimes occurred with the retention, and sometimes with the alteration, of the steric configuration. One was thus to a great extent deprived of the possibility of solving, with the help of classical organic chemistry, the problem of the steric relation between optically active substances, and, although the problem was for various reasons the object of lively interest, for a long period no other methods were available. A special circumstance that arises in such configurational determinations may be worth pointing out: the nature of the problem offers only two alternatives, the same or opposite configurations. A hypothesis or method that lacks any basis of reality may give here correct or false results with equal ease. This sphere of research became increasingly characterised by ambiguity and uncertainty.

More recently Freudenberg and W. Kuhn, by investigating the optical activity over a wide spectral range or in a series of derivatives of a basic substance, have in many cases been able to draw far-reaching conclusions regarding the steric relationships, especially for closely related compounds. Kuhn also, partly building on the work of earlier investigators, has subjected optical activity to a thorough theoretical treatment, and considers, in certain cases at least, that he has found a fundamental solution to the problem of absolute configuration (2).

The applicability of the optical methods is, however, often limited, and the ways in which other workers have applied the rules expounded by Freudenberg have given rise to criticism and contradiction in not a few cases.

From the chemist's point of view optical activity in itself is of secondary interest; it is certainly a very important diagnostic aid, but nevertheless has the character of an accessory phenomenon. From the chemical viewpoint the primary feature is the asymmetrical form of the molecule, for it is this which excerts a decisive influence on the reactivity and the possibilities of reaction in asymmetrical systems among which, inter alia, all living organisms must be counted. A method for the determination of configuration, based on the mutual reaction relationships of the asymmetrical molecules, in this case more specifically their power of forming molecular compounds or solid solutions, may therefore not be considered only as a control or complement to the optical methods. It also offers possibilities for the development and deepening of our knowledge of reactions in asymmetrical systems and thus for the clarification of one of the central problems of biochemistry.

It is well known that a pair of optical antipodes (enantiomorphs) often crystallise together to give a *racemic compound*. This consists of equal quantities of the two components and is clearly distinguishable from these by its physical properties. In the melting point curve it manifests itself by a special branch of the curve with a more or less clear maximum at 50 per cent of each component (cf. Figs. 1 and 9 below). As early as 1899 Centnerzwer (3) found that (+)-chlorosuccinic acid and (−)-bromosuccinic acid[1] give a molecular compound which must obviously be considered as a kind of racemic compound. In 1921 Delépine (4) took up the question of the existence of such molecular compounds for general discussion. Since the components here are not true enantiomorphs but only have very similar structures, the molecular compound must display optical activity, and for such com-

[1] The signs + and − always denote, in this paper, directions of rotation, without regard to configuration. In the example given, besides opposite directions of rotation, opposite configurations also occur.

pounds he proposed the term "racémiques actifs", which may be translated as "active racemic compounds". Neither of these workers appears, however, to have interested himself in the possibility of establishing in this way the configurative relationships between different optically active compounds. On the other hand, TIMMERMANS, who cites CENTNERZWER's work, has, since the end of the nineteen-twenties, investigated a number of systems with such an end in view (5, 6, 7, 8, 9, 10, 11, 12). In only relatively few cases, however, has he encountered molecular compounds, and in several of these the components have been so unlike chemically that it must be doubted whether the molecular compounds are really comparable with racemic compounds. A compound between dichlorosuccinic acid and lactamide (12) appears to me rather interpretable as a salt and hardly permits any conclusions regarding the relative configurations of the components. The investigations carried out during the last decade at the Laboratory for Organic Chemistry at Uppsala University appear, however, to show that the study of melting point diagrams, if proceeded with in a suitable manner, is a quite practicable method for the establishment of steric relationships.

By way of introduction, it seems desirable to touch upon a question of nomenclature. The term "racémique actif" is hardly a happy choice. Among other things it may easily lead to confusion with the cases when two enanthiomorphs give molecular compounds in proportions other than 1 : 1 (anomalous racemic compounds). Such a case is described by BERGMANN (13). Several workers, e. g. LETTRÉ (14, 15, 16) and in his time also CENTNERZWER, have instead employed the term "partially racemic compound" ("partielles Razemat"), which was introduced by EMIL FISCHER (17), and originally signified a molecular compound between two diastereoisomeric substances. The term has, however, been criticised from the logical and linguistic points of view (18).

As it seems to me desirable to have an adequate term which does not possess a more limited significance in the older literature, I have proposed the term "*quasi-racemic compound*" (19) and thus characterise, in agreement with a definition formulated by LETTRÉ (16), a molecular compound which may be

considered to be derived from a true racemic compound by a not too extensive change in one of the components.

The possibilities for the formation of a quasi-racemic compound are dependent upon a number of factors. The tendencies to form true racemic compounds may be very different even for closely related substances. Thus α-xanthogenpropionic acid (I) gives a racemic compound which melts at a consider-

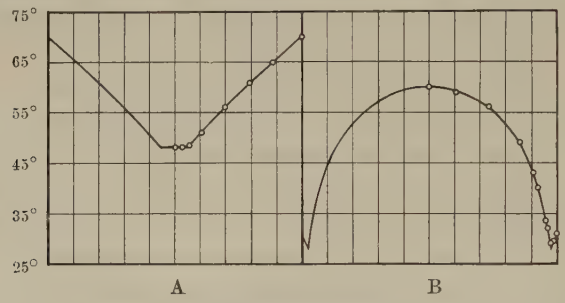
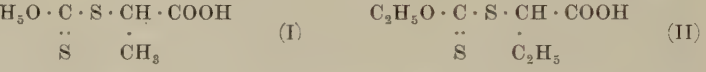


Fig. 1. A) (+)- and (−)-α-Xanthogenpropionic acid. B) (+)- and (−)-α-Xanthogen-n-butyric acid.

ably lower point than the enanthiomorphs and only indicates its presence within a very limited portion of the melting point



curve (Fig. 1 A). The next higher homologue, α-xanthogen-n-butyric acid (II) behaves in a directly opposite manner, the molecular compound completely dominating the diagram (Fig. 1 B). It is clear that the latter acid should have a greater tendency to enter into quasi-racemic compounds than the former (20).

It may also be asked how great the structural difference between the two components may be, that the power of forming quasi-racemic compounds may not be lost. A certain indication should first be given in this matter by the power of different atoms and atomic groups to replace one another in an isomorphous mixture. It has, however, been shown that quasi-racemic compounds occur in many cases where the enanthiomorphs of the *same* configuration are not isomorphous. In some cases we have obtained molecular compounds even

between the first optically active members of a homologous series.

In many cases the question naturally arises how it shall be decided in practice whether a molecular compound between two optically active substances is really to be considered as a quasi-racemic compound. In the first place, each component must form a molecular compound only with one antipode of the other. If compounds are obtained with both antipodes, it is clear that steric factors are of subordinate importance in the formation of the compounds. In addition crystallographic relationships should be sought for between the quasi-racemic compounds and the true racemic compounds of the components. In many cases it is most simple to investigate, with the help of melting point curves, whether it forms a solid solution with either of these, but X-ray diagrams may frequently prove to be of value.

If two compounds are too different to give a quasi-racemic compound, the question of configuration may be solved by comparing both with a suitably chosen third substance. Another method is to introduce a common large substituent into both substances (the centre of asymmetry must naturally remain unaffected); the structural difference is thus rendered less prominent. This method may also be employed with advantage if the two compounds, on account of their physical properties (low melting point, small crystallisation power etc.) do not lend themselves to the recording of melting point curves.

A review will now be given of the results hitherto obtained, together with examples of the modes of procedure in different cases.

It is well known that analogous compounds of *sulphur* and *selenium* are often isomorphous. The possibility of obtaining quasi-racemic compounds has been tested in seven cases (21, 22, 23, 24, 25, 26). A positive result was obtained in each case. Here the configuration determination presents no difficulties. In some cases, for example that of the hydrochloride of cystine and its selenium analogue (23), which do not exhibit well-defined melting points, the question could not be decided by melting point curves, but other methods were resorted to (solubility

determinations, examination of crystals under the polarising microscope).

A direct comparison between *oxygen* and *sulphur* compounds appears on the whole impossible since the atomic radii of oxygen and sulphur are too unlike (0.66 and 1.04 Å respectively) and the difference in the external dimensions of the molecules is thus too great. For the correlation of *malic acid* (III) and

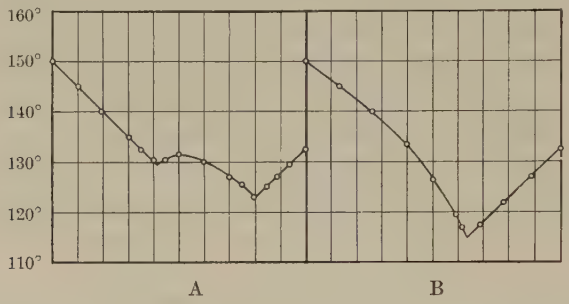
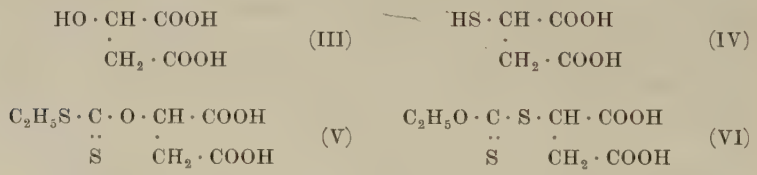


Fig. 2. A) (+)-Ethyl-carbothiolone malic acid and (+)-Xanthogensuccinic acid. B) (+)-Ethyl-carbothiolone malic acid and (−)-Xantogensuccinic acid.

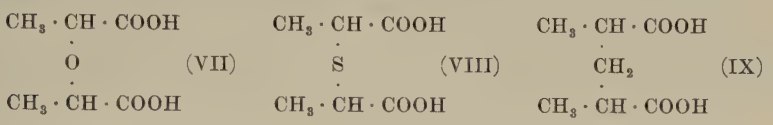
mercaptosuccinic acid (IV) I have therefore chosen two derivatives of these compounds, ethylcarbothiolone malic acid (V) and xanthogensuccinic acid (VI) which are isomeric and only differ in the relative positions of a sulphur and an oxygen atom. Fig. 2 shows that the two acids, which have the same direc-



tion of optical rotation, give a molecular compound and therefore must be assigned opposite configurations. The relationships of these acids to the parent substances can easily be established by purely chemical methods; the final result is that malic acid and mercaptosuccinic acid, having the *same* direction of rotation, also have the *same* configuration (27).

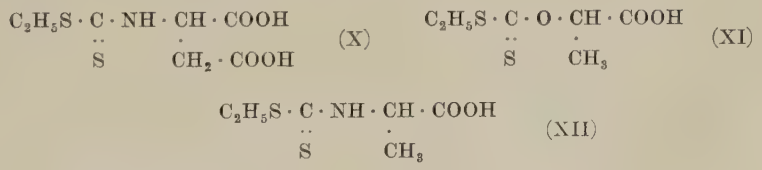
Lactic acid and *thiolactic* (*mercaptopropionic*) *acid* were investigated with the aid of their derivatives dilactic acid (VII)

and thiodilactic acid (VIII). These acids definitely gave no molecular compounds, but since the atomic radius of carbon



(0.77 Å) lies between those of oxygen and sulphur, it might be hoped that both would give quasi-racemic compounds with $\alpha\alpha'$-dimethylglutaric acid (IX). This proved to be the case, the result of the investigation being that (+)-*lactic acid* and (—)-*thiolactic acid* were shown to have the *same* configuration (28).

Hydroxy- and amino-acids are too unlike in respect of the polar properties of their molecules for it to be prudent to draw definite conclusions from their melting points curves. As is well known, amino acids are considered usually to occur in the lattice as "zwitterions". By the introduction of a suitably chosen substituent at the hydroxy and amino groups, however, it is possible simultaneously to increase the relative structural similarity and suppress the basic character of the amino group. The previously mentioned ethylcarbothiolone malic acid (V) gives, with a derivative of aspartic acid, ethyl-dithiocarbamino-succinic acid (X), a quasi-racemic compound (Fig. 3), from which it could be deduced that (—)-*malic acid* and (+)-*aspartic acid* have the same configuration (29).



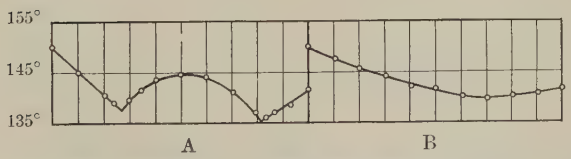


Fig. 3. A) (+)-Ethyl-carbothiolone malic acid and (—)-Ethyl-dithiocarbamino-succinic acid. B) (+)-Ethyl-carbothiolone malic acid and (+)-Ethyl-dithiocarbamino-succinic acid.

In the same manner it was established with the help of acids (XI) and (XII) that (+)-*lactic acid* has the same configuration as (+)-*alanine* (30). Agreement is shown in both cases with the results obtained by an optical method by Freudenberg (31, 32, 33). Since the method gives positive results even for the simplest optically active amino acid, alanine, there is reason

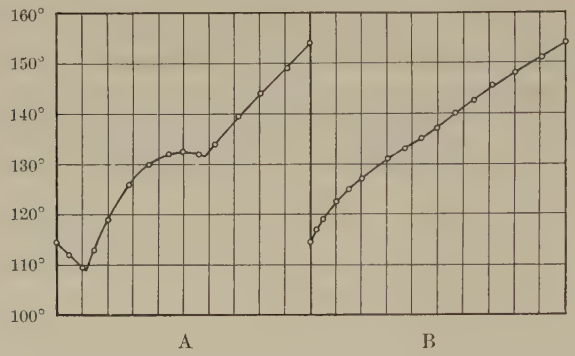


Fig. 4. A) (−)-Methylsuccinic acid and (+)-Mercaptosuccinic acid.
B) (+)-Methylsuccinic acid and (+)-Mercaptosuccinic acid.

to believe that it is generally applicable for the correlation of other amino acids of the type $R \cdot CH(NH_2) \cdot COOH$ with the corresponding hydroxyacids.

By the introduction of the group $C_2H_5S \cdot CS \cdot$ it proved possible to correlate two homologous optically active hydroxyacids, namely *lactic acid* and *α-hydroxy-n-butyric acid*, whose steric relationships have been the object of discussion (34). It proved that the acids, which in dilute aqueous solution rotate polarised light in the *same* direction, have *opposite* configurations. This is in agreement with the opinion of Szarvas (35).

Special interest is associated with the steric relationships of halogen compounds, since these are often employed as starting materials in the preparation of other substances, and are the classical objects for the study of the Walden inversion. Here a direct study of the melting point curves is often excluded on account of the reactivity of a halogen compound towards, for example, mercapto groups. Instead the relationship of both compounds to the more indifferent methyl derivatives may be studied.

Mercaptosuccinic acid (IV) and *methylsuccinic acid* (XIII), when they have opposite modes of rotation, give a molecular compound 1 : 1. Acids of the same mode of rotation, on the other hand, give a melting point curve which shows mutual but not unlimited miscibility in the solid phase (Fig. 4). Obviously we have in the latter case a curve of the kind designated by Roozeboom (36) as Type 4. The two dextrorotatory acids thus have the same configuration (37). Especially interesting are the curves obtained with on the one hand methylsuccinic acid, and on the other hand chlorosuccinic acid (XIV) and bromosuccinic acid (XV). Several cases are known where the methyl group of organic compounds in isomorphus mixture can replace chlorine and bromine (38, 39). If active methylsuccinic acid is mixed with small quantities of halosuccinic acid of opposite mode of rotation, the melting point sinks towards a eutectic (Figs. 5 A

$CH_3 \cdot CH \cdot COOH$ (XIII) $Cl \cdot CH \cdot COOH$ (XIV) $Br \cdot CH \cdot COOH$ (XV)
$CH_2 \cdot COOH$ $CH_2 \cdot COOH$ $CH_2 \cdot COOH$

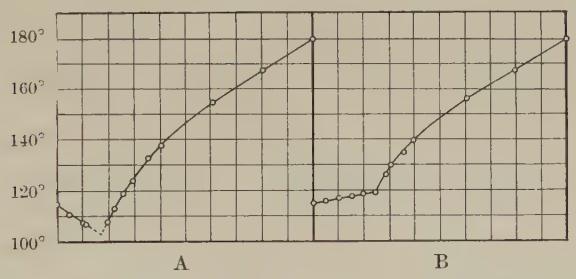


Fig. 5. A) (+)-Methylsuccinic acid and (−)-Chlorosuccinic acid. B) (−)-Methylsuccinic acid and (−)-Chlorosuccinic acid.

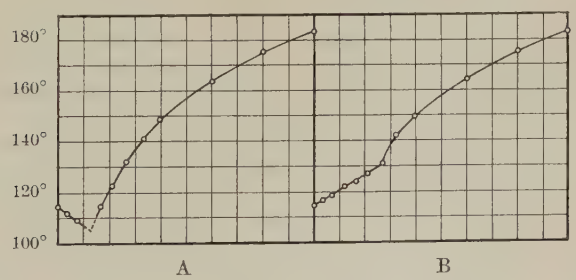


Fig. 6. A) (+)-Methylsuccinic acid and (−)-Bromosuccinic acid. B) (−)-Methylsuccinic acid and (−)-Bromosuccinic acid.

and 6 A). If, on the other hand, halosuccinic acid of the *same* mode of rotation is added, the melting point rises, which shows that the halo-acid enters into solid solution (Figs. 5 B and 6 B). Here, also, it is obvious that diagrams of Roozeboom's Type 4 occur and one should be justified in concluding that the antipodes which form solid solutions have similar configurations. Finally it follows that a mercaptosuccinic acid and a halosuccinic acid with the *same* mode of optical rotation are also *similar in the configurative respect.* By the study of the course of the reaction, very complicated in this case, when the halogen is substituted by a sulphur-containing group, Holmberg has earlier come to the same conclusion (41).

On oxidative degradation of optically active natural products, e. g. terpenes, optically active alkyl succinic acids or alkyl glutaric acids are frequently obtained. Since these acids lack characteristic absorption bands (with the exception of those deriving from the carboxyl group), difficulties are encountered in correlating, by optical methods, their configurations with those of other groups of substances. It is therefore of interest that, as we have seen above, both methylsuccinic acid and dimethylglutaric acid could be sterically joined to the mercapto acids and thus to the hydroxyacids.

The work now progressing is concerned partly with gaining control and increased certainty, by examining some new representative cases, of the steric connections between different groups of compounds and partly with investigating more closely

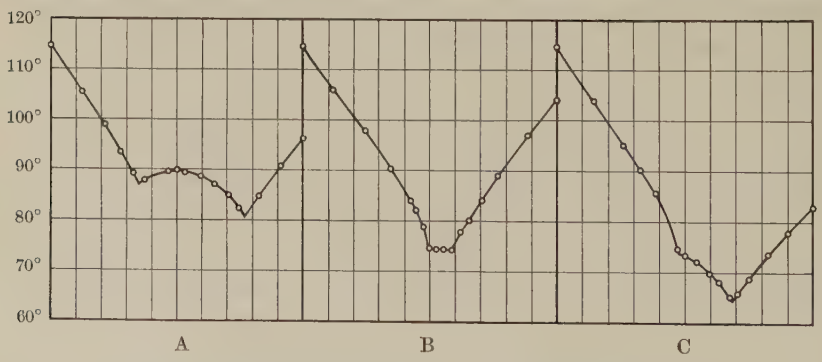


Fig. 7. A) (+)-Methylsuccinic acid and (−)-Ethylsuccinic acid.
B) (−)-Methylsuccinic acid and (+)-n-Propylsuccinic acid.
C) (−)-Methylsuccinic acid and (+)-n-Butylsuccinic acid.

the relationships of the homologues of succinic acid and glutaric acid. In this sphere a paper by Timmermans (11) is already available. This worker claims to have found a compound of (+)-propyl- and (−)-hexylsuccinic acid. Since his data concerning the physical constants of propylsuccinic acid differ greatly from my own observations, I find it difficult to give a definite opinion regarding his results. It seems, however, that the alkylsuccinic acids constitute very suitable objects for the study of the conditions leading to the formation of quasi-racemic compounds between the different members of a homologous series. Methylsuccinic acid gives a very beautiful curve with ethylsuccinic acid, showing the presence of a molecular compound 1 : 1, and even with the active n-propyl and n-butyl derivatives distinct phases are obtained in the region of 50 mol. per cent (Fig. 7). Ethyl- and n-propylsuccinic acids also give a molecular compound (Fig. 8), but this does not play such a prominent rôle in the diagram as the compound between methyl- and ethylsuccinic acids (Fig. 7 A). It is interesting to compare these curves with Fig. 9 which illustrates the tendencies of the three alkylsuccinic acids to form true racemic compounds. This tendency appears to be greatest for the ethyl and least for the propyl derivative, where the racemic compound melts about 10° lower than the antipodes. This is certainly the explanation for the fact that the quasi-racemic

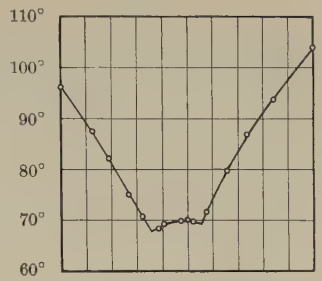


Fig. 8. (−)-Ethylsuccinic acid and (+)-n-Propylsuccinic acid.

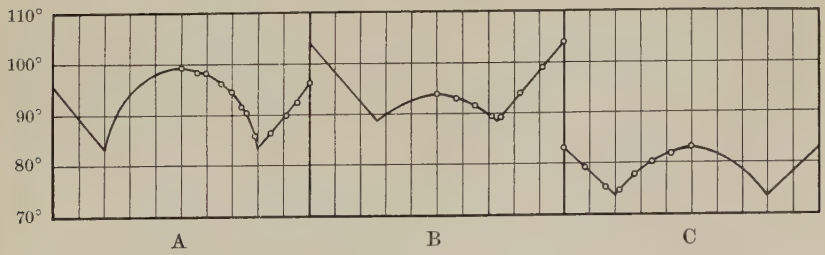


Fig. 9. A) (+)- and (−)-Ethylsuccinic acid. B) (+)- and (−)-n-Propylsuccinic acid. C) (+)- and (−)-n-Butylsuccinic acid.

compounds in which n-propylsuccinic acid is one of the components have relatively low melting points and play a quite minor rôle in the melting point curve (42).

It may finally be mentioned that alkylsuccinic acids with normal carbon chains can give quasi-racemic compounds with those where the chains are branched. Thus a molecular compound has been obtained between (+)-n-butylsuccinic acid and (—)-isobutylsuccinic acid (43). In the case of all alkylsuccinic acids investigated, antipodes with the same mode of rotation appear to have also the same configuration.

The preparation of optically active compounds in the sterically quite pure state is often a laborious task which may require great preparative experience. It is therefore natural that investigations of the type reviewed here make considerable demands on time. On the other hand this research, as has already been stated in the introduction, has an importance beyond the simple purpose of determining configuration. Lettré (15, 16), has drawn parallels between the quasi-racemic compounds (called by him "partielle Razemate") and the complexes formed between enzymes and their substrates or between antigens and antibodies. In the formation of the latter compounds it is well known that steric factors play a great part. From this point of view every contribution to our knowledge of the mutual reactions of asymmetrical molecules, and, not least, of the powers of different atoms and groups of atoms to replace each other in the same environment, is of no small interest.

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High-Molecular Wood Celluloses.

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The isolation of cellulose from wood involves the breaking of bonds between the cellulose and the other constituents of wood, lignin or polysaccharides. In all the technical isolation processes, some of the bonds of the cellulose itself are also broken, thus causing depolymerisation of the cellulose molecules. Isolated wood celluloses have lower molecular weights than native fibre celluloses, e. g. cotton, flax and nettle fibres (Gralén and Svedberg (1), Gralén (2)). The question is still open, whether the molecules of the cellulose of wood in its native state are as large as, or smaller than, those of the native plant fibres.

Attempts have been made earlier to isolate the cellulose of wood with the least possible disintegration of the molecules. The treatment of wood with chlorine dioxide (3) or sodium chlorite (4, 5) has been recommended. We have tried sodium chlorite, but found that it caused some depolymerisation, probably by oxidation (2). Jahn and Coppick (6) reported the nitration of wood. Finally, the treatment of wood with cuprammonium has offered some possibilities (2). The two last-mentioned methods do not, however, give a complete isolation.

The technical sulphite process is a very mild way of isolating the cellulose, and we have found it most suitable for our purposes. In the following account some results of these investigations will be reported.

Materials Investigated.

Most of the preparations were taken from a single technical sulphite cooking of spruce wood in a container of 350 m^3

capacity. The cooking liquor contained 0.86 per cent CaO and 5.95 per cent SO_2. Samples (E—L) were removed through a lock at different times after the start. Fig. 1 gives the temperature scheme of the cooking process.

Some other preparations were made in a small glass autoclave (volume 200 ml.) in the laboratory. It was filled with 23.5 g. splints, cut on a milling machine, and 190 ml. calcium bisulphite solution (0.85 % CaO, 6.0 % SO_2). The temperature was raised to 100° during 4 hours, just as in the technical

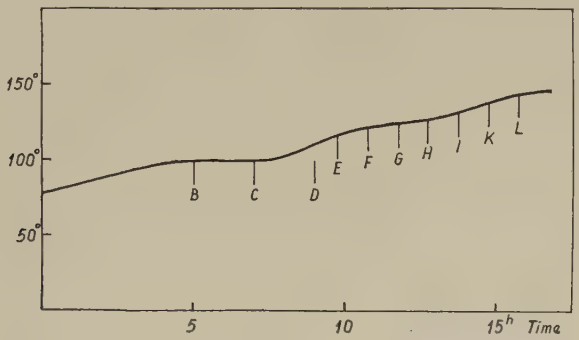

Fig. 1. Temperature scheme of sulphite cooking.

process, and different preparations were kept at that temperature for 1, 3, and 5 hours (B, C, and D, see Fig. 1). Untreated wood splints were also investigated (A).

Table 1 gives the analyses of the samples.

The samples were washed with water and dried at room temperature. The samples B—G had a distinct wood structure, but were softer and could be more easily split up than the untreated wood. Some wooden splints remained, however, even after defibration in water and in a dry defibrator. The sample E was fractionated in a dry state by sieving. About 30 per cent passed through a 30 mesh sieve (E I) and 15 per cent through 40 mesh (E II). These fractions contained less wood splints than the original E, and seemed to consist mostly of pure cellulose fibres.

The disintegration of the wood structure proceeded during the cooking process, and the last two samples were completely defibrated on violent stirring with water. It should be men-

Table 1.

Sample	Time after start of the sulphite process	Lignin, per cent	Pentosan, per cent
A	0^h	28.8	—
B	5^h	25.5	—
C	7^h	24.6	—
D	9^h	22.6	—
E	$9^h\,45^m$	16.6	4.82
F	$10^h\,45^m$	16.2	4.65
G	$11^h\,45^m$	11.9	4.70
H	$12^h\,45^m$	6.1	4.84
I	$13^h\,45^m$	3.7	4.60
K	$14^h\,45^m$	2.4	4.58
L	$15^h\,45^m$	2.1	3.60

tioned that the cooking process was finished in 19 hours. The resultant cellulose then contained about 0.9 per cent lignin.

For the investigation of the molecular weights it is necessary to bring the cellulose into solution. There are no simple solvents available for cellulose. Cuprammonium is a good solvent, but its complex nature causes practical and theoretical difficulties in the molecular weight determinations (Kraemer (7), Gralén (2)). According to Staudinger (8), cellulose can be nitrated without depolymerisation, and the solution of the nitrate in acetone or another organic solvent is a better object than the cuprammonium solution for ultracentrifuge and diffusion experiments. Staudinger's statement has not quite been confirmed, but the nitration seems to entail a constant depolymerisation (cf. Gralén (2)). In an earlier publication (2), one of us used the nitration mixture 40 % HNO_3, 40 % H_3PO_4, 20 % P_2O_5. As shown by Bouchonnet *et al* (9), a mixture containing more HNO_3 and less P_2O_5 is more fluid, gives a more homogeneous nitration, and is easier to wash away after the nitration, local heating thus being avoided. We used the reagents mentioned in the proportions 48:50:2 (cf. Davidson (10)). The nitration was performed at 0° for 4 hours, and the cellulose nitrate was washed with cold (— 10°) 50 per cent acetic

acid and large volumes of water. It was stabilised by boiling 4 times for half an hour with water.

The incompletely disintegrated wood samples (A—H) had a brown to yellow colour, On nitration, the nitration acid became brown, probably because some of the lignin was destroyed and dissolved in the acid. On the nitration of untreated wood, traces of nitrous gases appeared, but not with any other sample. The nitrates were also rather coloured, but most of the colour dissolved in the water during the boiling for stabilisation. From the samples E and H about 23 and 8 per cent respectively disappeared in the acid and the water in this way. The dissolved parts probably consisted mostly of lignin, nitrated or decomposed.

The cellulose nitrate of A was soluble to about 40, B to about 50, C to 92 per cent in acetone. The nitrates of D and the later samples were completely soluble. Butyl acetate dissolved the nitrates of E and F only to 88 and 99 per cent respectively. It is thus a less effective solvent than acetone. It is seen that the earliest samples are less soluble, but the nitrates obtained are already completely soluble after a very mild sulphite treatment, although only a relatively small amount of the lignin of the wood has been dissolved by the sulphite process.

The solubilities in cuprammonium are given in Table 2. A more prolonged action of the sulphite is needed to give complete solution in cuprammonium. It is of interest to note that the sieved samples E I and E II are more soluble than their origin E.

Table 2. Solubility in Cuprammonium.

Sample	Per cent dissolved
E	42
E I	58
E II	65
F	52
G	80
H	93
I	100
K	100
L	100

Viscosity Measurements.

Viscosity measurements were performed in cuprammonium with complete exclusion of air. The experimental arrangements described by Gralén (2) were used. The results are given in Table 3 and Fig. 2.

Table 3. Viscosity Measurements in Cuprammonium.

Sample	$\lim_{c \to 0} \frac{\log \eta/\eta_0}{c}$
E	7.1
F	7.4
G	9.5
H	9.9
I	8.7
K	7.9
L	6.8

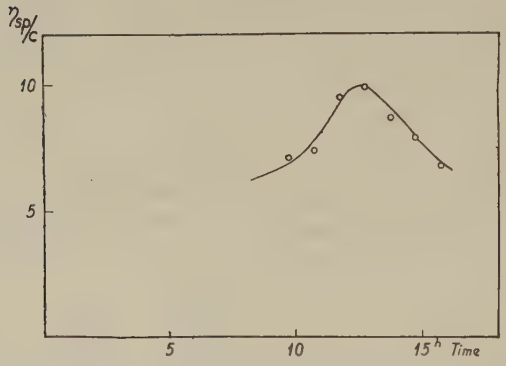

Fig. 2. Variation in the viscosity of the cellulose in cuprammonium with time of sulphite cooking.

The curve of Fig. 2 is of special interest. It shows a maximum at about that point of the process where the action of the sulphite has proceeded so far that complete solution of the cellulose in cuprammonium is obtained. The lower viscosities of the earlier preparations are explained by the fact that the cellulose dissolved is not an average of the total. The smaller molecules are preferentially dissolved, and the viscosity

is thus lower than the average. The descent of the curve after the maximum is due to depolymerisation of the cellulose by the sulphite action.

The viscosities of the nitrates in acetone show a similar curve. The maximum is at an earlier stage, which corresponds to the fact that complete dissolution of the nitrates is attained earlier (cf. p. 277).

Sedimentation and Diffusion Measurements on the Cellulose Nitrates.

The sedimentation diagrams of the cellulose nitrates in acetone show two components, of which cellulose sediments the

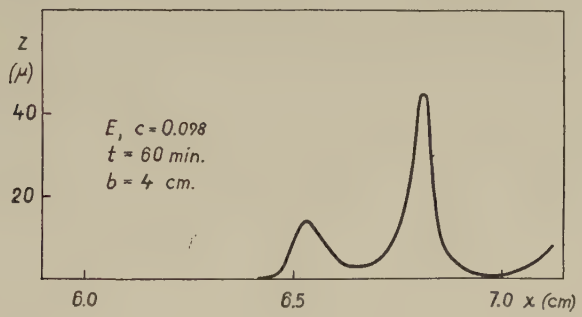

Fig. 3. Sedimentation diagram of cellulose nitrate from sulphite cooking.

fastest. The slower component is probably part of the cellulose together with some hemicellulose (cf. Gralén (2)). A typical diagram is given in Fig. 3. By integration of the curve it is found that the cellulose component is about 70—75 per cent of the total dissolved substance, in the later preparations a little more.

The polydispersity of the material has been estimated by the width method of Gralén (2). It is given in terms of dB/dx, the variation of the curve width with the distance that has been covered by sedimentation. The quantity dB/dx has been calculated partly for the whole sedimentation curve (dB/dx_{tot}), partly for the faster sedimenting component (dB/dx_{cell}). The results of the sedimentation measurements are given in Table 4.

Table 4. Sedimentation Measurements on Cellulose Nitrates.

Sample	c (g./100 ml.)	s_{20} (SVEDBERG units)	$\left(\frac{dB}{dx}\right)_{cell}$	$\left(\frac{dB}{dx}\right)_{tot}$
A	0.136	12.1	—	—
	0.069	16.3	—	—
	0.034	19.6	—	—
	0	*23.3*	—	—
B	0.100	14.4	—	0.50
	0.050	16.9	—	0.60
	0	*20.5*	—	*0.74*
C	0.100	14.4	—	—
	0.050	16.0	—	—
	0	*18.0*	—	—
D	0.100	13.1	0.35	0.50
	0.050	15.3	0.45	0.65
	0	*18.4*	*0.60*	*0.85*
E	0.150	12.5	0	0
	0.098	14.9	0.07	0.10
	0.068	18.4	0.22	0.30
	0.039	21.2	0.36	0.52
	0	*29.3*	*0.56*	*0.83*
E I	0.206	10.0	0	0
	0.076	15.2	0.15	0.21
	0.068	17.0	0.18	0.26
	0.058	18.4	0.22	0.31
	0.052	19.0	0.25	0.36
	0.041	20.1	0.27	0.38
	0.030	24.6	—	—
	0	*33.5*	*0.41*	*0.58*
F	0.150	11.6	0	0
	0.099	13.9	0.05	0.06
	0.069	17.6	0.13	0.18
	0.039	20.9	0.38	0.49
	0	*28.7*	*0.73*	*0.92*
G	0.151	11.9	0	0
	0.100	14.5	0.05	0.06
	0.069	16.9	0.17	0.22
	0.040	19.3	0.40	0.53
	0	*26.5*	*0.73*	*0.94*
H	0.149	11.4	0	0
	0.106	13.0	0.05	0.07
	0.075	14.7	0.12	0.17
	0.041	18.5	0.37	0.50
	0	*24.7*	*0.67*	*0.91*
I	0.150	11.7	0	0
	0.100	13.7	0.08	0.11
	0.083	14.4	0.18	0.26
	0.049	18.3	0.30	0.43
	0.040	19.2	0.35	0.50
	0	*24.2*	*0.55*	*0.79*

Table 4 (contin.)

Sample	c (g./100 ml.)	s_{20} (SVEDBERG units)	$\left(\frac{dB}{dx}\right)_{cell}$	$\left(\frac{dB}{dx}\right)_{tot}$
K	0.153	10.6	0	0
	0.104	13.8	0	0
	0.064	16.0	0.23	0.31
	0.052	18.1	0.32	0.43
	0.039	19.1	0.39	0.53
	0	*25.0*	*0.61*	*0.82*
L	0.150	11.7	0	0
	0.100	13.4	0.10	0.13
	0.070	16.8	0.22	0.28
	0.040	19.7	0.39	0.50
	0	*26.2*	*0.56*	*0.71*

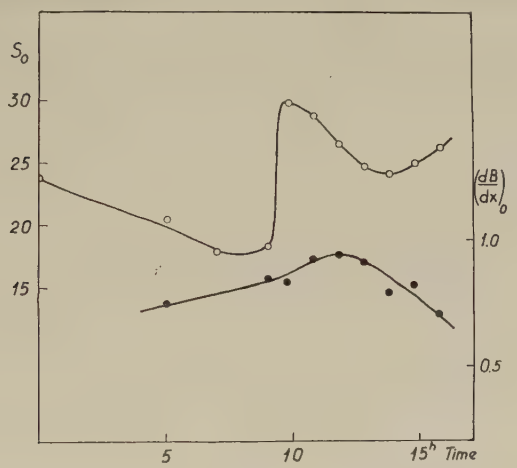

Fig. 4. Variation in s_0 and $\left(\frac{dB}{dx}\right)_0$ with time of sulphite cooking.

The extrapolation of the s- and $\frac{dB}{dx}$-values has been made according to the methods given by GRALÉN (2). The variation of s_0 and $(dB/dx)_0$ with the time of cooking is given in Fig. 4. Both the sedimentation constant and the polydispersity pass through a maximum.

The diffusion measurements were made in a glass cell at 20°. The experimental arrangements have been described earlier (2). The calculation of the results was performed according to the theories developed by GRALÉN (2). By the formula

$$D_m = \frac{m_2}{2\,t\,A}$$

an average value of D for the polydisperse system is obtained. Here m_2 signifies the second moment of the curve about the arithmetic mean, t is the time after the start, and A is the area between the curve and the x-axis. Another average is given by

$$D_A = \frac{A^2}{4\,\pi\,H^2\,t}$$

where H is the maximum ordinate of the curve. The ratio D_m/D_A is a measure of the polydispersity. From the skewness of the curve the dependence of D on the concentration and thus the diffusion constant at zero concentration, D_0, can be determined. For details the reader is referred to the original work (2). The results of the measurements are compiled in Table 5. The diffusion constants are all given in units of 10^{-7} cm^2/sec.

Table 5. Diffusion Measurements on Cellulose Nitrates.

Sample	D_m	D_A	D_0	D_m/D_A
C	1.64	1.37	1.09	1.20
D	1.80	1.61	1.14	1.12
E	0 97	0.93	0 50	1.04
E I	1.22	1.11	0.86	1.10
F	1.25	1.10	0.81	1.14
G	1.35	1.07	1.01	1.26
H	1.75	1.60	1.13	1.09
I	1.61	1.28	1.13	1.26
K	2.05	1.53	1.75	1.34
L	2.16	1.94	1.82	1.11

Molecular Weights.

The molecular weights were calculated according to Svedberg's formula

$$M = \frac{R\,T\,s}{D(1 - V\varrho)}$$

using the extrapolated values s_0 and D_0. $V = 0.51$ (Scholten (11)), $\varrho = 0.792$. The values obtained are given in Table 6.

Table 6. Molecular Weights of Cellulose Nitrates.

Sample	$M \times 10^{-3}$	Degree of polymerisation (D. P.)	f/f_0
C	670	2 500	11.1
D	660	2 400	11.5
E	2 440	9 000	16.8
E I	1 590	5 900	11.3
F	1 450	5 300	12.4
G	1 070	3 800	11.0
H	890	3 200	10.4
I	880	3 100	10.5
K	580	2 000	7.7
L	590	2 000	7.4

The variation in the degree of polymerisation of the dissolved cellulose nitrates during the cooking proces is given in Fig. 5. This curve is very similar to that of Fig. 2, showing a maximum at the point where the possibility of complete dissolution is reached. It is obvious that an incomplete dis-

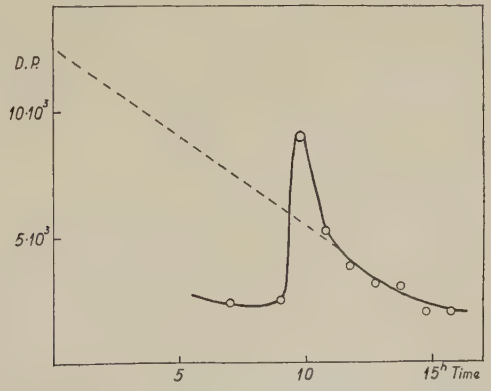

Fig. 5. Variation in the degree of polymerisation with time of sulphite cooking.

solution leaves the larger molecules undissolved, and the solution obtained contains only smaller molecules. Some depolymerisation on the nitration of samples with high lignin content is also conceivable. The highest molecular weights are obtained for the sample E, 9 3/4 hours after the start of the cooking process. Extrapolation of the curve of Fig. 5 to zero time should give the D. P. of the cellulose in its native state in the wood. Of course this extrapolation is very uncertain, and it is questionable whether it is permissible. As the dotted line is drawn in Fig. 5, it gives a D. P. of 12 500 at zero time, i. e. of the same order of magnitude as for native cotton or ramie (Gralén and Svedberg (1)). It should be noted here that we are not sure that the nitration process employed does not involve some depolymerisation. Gralén (2) showed that the nitration with the 40:40:20-acid entailed breaking about 0.3 per mille of the glucose bonds. The depolymerisation effect of the acid used here, 50:48:2, is less, but probably not zero.

The Shape of the Cellulose Molecules.

The frictional ratios f/f_0 of the molecules, are given in the last column of Table 6. For a spherical molecule, f/f_0 is $= 1$, and

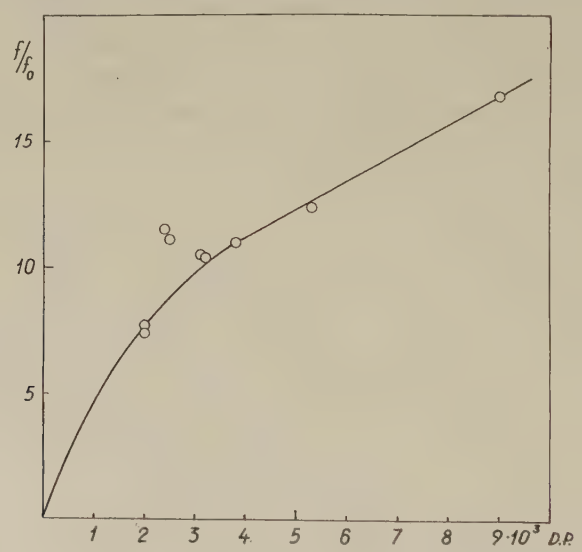

Fig. 6. The frictional ratio as a function of D. P. for the cellulose nitrates.

the magnitude of the ratio indicates the asymmetry of the molecules. In the case of unsolvated molecules with the shape of oblong rotational ellipsoids, $f/f_0 = 10$ means an axial ratio of 600. It is clear that the molecules of the cellulose nitrates have a thread-like shape, and the asymmetry increases with the molecular weight (Fig. 6). The most plausible deduction from the data reported here is that the molecules are slightly folded or undulate, unbranched chains of glucose units. Under certain assumptions it can be estimated that the length of the molecules of the sample E is about 0.002 mm. Such a molecule should be easily visible in a microscope, were it not so extremely thin.

The Polydispersity.

As a general rule for celluloses, the polydispersity increases on depolymerisation (2). This is true for the first stages of the sulphite process. In this part of the process, the attack of the hydrolysing sulphite is rather inhomogeneous, as the wood structure hides parts of the cellulose. Later, when the lignin has been largely removed, the action on the cellulose will be more uniform. A uniform depolymerising action would give a constant polydispersity. As Fig. 4 shows, there is even a small decrease. This means that the extremely large molecules are preferably attacked, and the distribution curve thus becomes narrower. It is also possible that the smallest molecules are depolymerised so far that they dissolve in the cooking liquor and thus escape observation. In any case there seems to be a homogenising effect of the sulphite process.

Discussion.

From a scientific point of view it is of great interest to note the very high molecular weights of the celluloses obtained by a very mild sulphite cooking without complete disintegration of the wood. The measurements reported here make it very probable that the cellulose molecules of wood are of sizes quite similar to those of the fibre celluloses in their native state. The mild sulphite process obviously decomposes the wood

structure by first acting upon the bonds between the cellulose and the other constituents of the wood. The partly decomposed wood has a spongy structure. At this stage of the process it is possible by relatively simple means to isolate the cellulose either by nitration (as cellulose nitrate) or by dissolution in cuprammonium. The solubility is determined by the structure of the sample, the lignin content, and the molecular weight of the cellulose. The nitration destroys the lignin, but the cuprammonium solution leaves the lignin rather unaffected (cf. Freudenberg (12)). Nitration is thus the more effective procedure of isolation. It is noteworthy that the cellulose nitrate dissolved in acetone from the nitrated sample D, when reprecipitated with water, does not redissolve completely. Obviously the precipitation gives a more compact layering of the molecules than that originally present in the wood.

It is obvious that we have not been able to prepare celluloses which reach the upper limit of the molecular size of cellulose in wood. In view of the very high values obtained, and the polydispersity, it is even possible to assume that some of the cellulose molecules are extended throughout the length of the single wood fibres.

Summary.

By a mild sulphite cooking, which is broken off before the complete disintegration of the wood structure, it is possible to obtain wood celluloses of very high molecular weights. The sulphite-treated wood is extracted with cuprammonium, or nitrated in a nitric acid-phosphoric acid mixture. The highest degrees of polymerisation obtained are about 9 000. This is the highest value yet found for wood cellulose, and the molecules are of the same order of size as those of native fibre cellulose. Nitration and extraction with acetone is a more effective mode of isolation than extraction with cuprammonium.

By polydispersity measurements it has been found that the sulphite process possibly has a homogenising effect on the cellulose, when most of the lignin has been removed from the wood.

In conclusion, we wish to thank Professor The Svedberg for suggesting this investigation and for stimulating discussions in the planning of the work. His interest in high molecular substances, especially the possibilities of bringing them into solution as mildly as possible in order to measure their native molecular properties, has been our greatest stimulant.

Our thanks are due also to the *Mo och Domsjö A.B.* for valuable cooperation and for financial assistance.

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Production of Vinyl Acetate from Acetylene and Acetic Acid in the Presence of the Mercury Salts of Complex Fluorine Acids.

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Vinyl acetate is a liquid with an ester-like odour, boiling at 73° C and easily polymerized by the influence of light, peroxides, etc. It is produced from acetylene and acetic acid in the presence of catalytic activators,

$$CH : CH + HOCOCH_3 \rightarrow CH_2 : CHOCOCH_3 + 28.3 \text{ kcal};$$

by which however primarily formed vinyl acetate may be converted into ethylidene diacetate by adding acetic acid,

$$CH_2 : CHOCOCH_3 + HOCOCH_3 \rightarrow CH_3 \cdot CH(OCOCH_3)_2 + 6.2 \text{ kcal}.$$

By varying the experimental conditions the conversion may be conducted so that either vinyl acetate or ethylidene diacetate is obtained as the main reaction product.

Here it is only possible to give a short historical account, especially devoted to the use of fluorine compounds as catalysts. For a closer study of the development we refer *i. a.* to Morrison and Shaw; "By-products of the carbide industry: the manufacture of ethylidene diacetate and vinyl acetate" (1).

Although ethylidene diacetate has been known since 1858, the direct manufacture from acetylene and acetic acid only dates from 1912, when Klatte obtained a patent (2) covering the adding of carbonic acids to acetylene in the presence of mercury salts, especially sulphate and phosphate. He observed that besides the esters of the hypothetic ethylidene glycol, also vinyl esters were formed, among them vinyl acetate, which does not seem to have been mentioned before. The catalysts

used by KLATTE were not particularly effective and were quickly consumed. About 1920, owing to the increased interest in ethylidene diacetate as a source for the manufacture of acetic anhydride, the problem of obtaining better catalysts and improved methods for the reaction between acetylene and acetic acid was taken up in several quarters.

During the first years no interest was shown for the vinyl acetate formed as a by-product, since its technical use was unknown. With the development of the chemistry of plastics around 1920 the demand for polymerisable substances increased, and investigations of the possibilities of obtaining vinyl acetate as the main product of reaction began.

For the reaction between acetylene and acetic acid two principally different main methods are industrially used, namely reaction in vapour phase at 200—300° C and in liquid phase at temperatures below the boiling point of acetic acid. According to the former method acetylene and vapours of acetic acid are led over carriers, impregnated with catalysts such as zinc- and cadmium acetate or phosphoric acid, for instance active carbon and silicagel (3). In this connection these methods are of little interest, so their mention here is unnecessary.

As far as the reaction in liquid phase is concerned, the main problem has been to find highly active catalysts, which even at low temperatures work at a satisfactory velocity. The formation of ethylidene diacetate is here suppressed, and the life-time of the catalyst is considerably prolonged. The catalytic effect of mercuric sulphate and phosphate is so low that the reaction must be carried out at such a high temperature, that the formation of ethylidene diacetate and tarry products is strongly favoured and the catalyst rapidly consumed by the reduction of the mercury salt.

Mercury salts of the sulphonation products of acetic acid show a far better activity (4). These catalysts are obtained by sulfonation of acetic acid with oleum or pure sulphur trioxide and partial neutralization of the sulphonation product with mercury oxide. If the reaction takes place at low temperature, mainly acetyl sulphuric acid, $CH_3 \cdot COOSO_3H$, is formed, while at a high temperature sulfoacetic acid, $HO_3S \cdot CH_2COOH$, is obtained as the main product. These catalysts allow reaction

at 30—50° C, but under their influence the vinyl acetate formed rather easily adds acetic acid, thus producing ethylidene diacetate. In order to obtain a good yield of vinyl acetate at a high degree of conversion it is therefore necessary successively to remove vinyl acetate from the solution, which may be done by the circulation of a large excess of acetylene through the liquid under continuous separation of the evaporated vinyl acetate.

In a patent published in 1933 Nieuwland (5) proposes mercury salts of fluoboric and fluosilicic acids as catalysts for the adding of organic compounds to acetylene, but in the patent carbonic acids were not expressly mentioned. The catalysts are produced by passing boron- or silicon fluoride into methanol or ethanol, whereby according to Nieuwland fluoboric acid and alkyl borate or fluosilicic acid and alkyl borate are formed. The acids so formed are neutralized by mercury oxide, whereupon the solution is added to the agent to react with acetylene. According to the examples mentioned, the consumption of mercury, however, is fairly high.

Furthermore in 1933 Weibezahn (6) published a patent proposing a catalyst consisting of boron fluoride and a mercury compound, the use of which, however, is limited to the production of vinyl esters. A subsequent patent (7) emphasizes that a considerably improved catalyst is obtained if, besides boron fluoride, hydrogen fluoride acid also is added to the reaction mixture. According to the examples about 4 g HgO, 1—1.5 g BF_3 and 0.5—1.0 g HF are used per kg acetic acid in the solution. While the mixture is vigorously stirred, acetylene is passed in at 30—35° C and is completely absorbed and converted. After a few hours the absorption stops, but it is not mentioned, whether this is due to the consumption of the catalyst or of the acetic acid. When the reaction is complete, the catalyst is destroyed by adding dry sodium acetate. After that the vinyl acetate is separated by distillation. Calculated on converted acetylene a yield of about 80 per cent vinyl acetate is obtained, but the converted quantity of acetic acid present is not mentioned.

According to a more recent patent (8) it is preferable to avoid the use of boron fluoride, directly forming the catalyst

in the solution by conversion between mercury oxide, hydrogen fluoride acid and boric acid or boron oxide (B_2O_3). The catalyst so produced is at least as active as the one produced with boron fluoride.

In a more recent patent Nieuwland (9) has also developed the use of boron fluoride by using a dihydroxy fluoboric acid, for which he gives two different methods of production. According to one of the methods the acid is obtained through the conversion between boron fluoride and boric acid in the presence of an inert solvent according to the following probable equation:

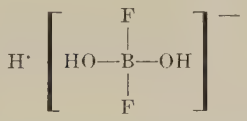
$$BF_3 + 2\,H_3BO_3 \rightarrow H_3BO_2F_2 + 2\,HBO_2 + HF.$$

At the end of the reaction the rather stable complex acid is distilled off from the metaboric acid. The acid may also — which is simpler — be produced through the conversion between boron oxide and dry hydrogen fluoride acid according to the equation:

$$9\,H_2F_2 + 4B_2O_3 \rightarrow 6H_3BO_2F_2 + 2\,BF_3.$$

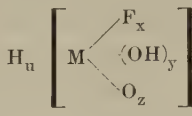
Working at low temperature, boron fluoride is bound to the formed acid but evaporates on distillation. The mixture, however, may be used as a catalyst as well as the free acid, i. e. after neutralization by mercury oxide.

According to Nieuwland the complex acid consists of dihydroxy fluoboric acid, for which he gives the following coordination formula:



When we started experimental work on the manufacture of vinyl acetate, the method suggested by Weibezahn, using mercury oxide, hydrogen fluoride acid and boric acid seemed particularly convenient, as the manufacture of vinyl acetate might be carried out in a comparatively simple apparatus and in a moderate scale. A test of the method furthermore gave satisfactory results, if the process was carried out in complete absence of water. As the method was protected by patent in

Sweden, the question arose, as to whether any other element than boron would give highly active complex acids together with hydrogen fluoride, which is fairly easy to produce. It is well-known that hydrogen fluoride acid dissolves many oxides or oxygen acids forming complex acids, the co-ordination formula of which may be summed up as follows:



where between the main valency number n of the element M and the indices u, x, y and z the following relation prevails:

$$u + n = x + y + 2z.$$

y and/or z may be $= 0$, thus obtaining the following subformulas:

$$H_u[MF_x]; \quad H_u[MF_x(OH)_y]; \quad H_u[MF_xO_z].$$

These types of acids may be obtained from a number of elements, but among these phosphorus and arsenic seemed particularly interesting, their complex acids showing great resemblance to the boron fluoride acids and their acids or anhydrides also being rather easily dissolved. On account of this their fluorine acids as well as those of the boron would readily be formed directly in the solution. These assumptions have been fully confirmed by our experiments, as shown by the following. The fluor arsenic acids have proved particularly useful and have for some years been used by us as catalysts with very good results in the technical production of vinyl acetate. Patents covering the use of the complex fluorine acids as catalysts for the production of vinyl esters have been applied for in many countries and up to now been granted *i. a.* in Sweden (10). Experiments are going on concerning the possibilities of using these compounds as catalysts for the addition of other organic compounds to acetylene and other conversions, but because of patent considerations it is not possible to give an account of these experiments in this paper.

Experiments.

The reaction was carried out in a 3-tubulated Woulf-bottle, placed in a water bath, thus facilitating heating or cooling, when required. The bottle was fitted with a fast gas-tight agitator, thermometer and in- and outlets. The acetylene was taken from a dissous gas container or a small transportable acetylene producer and was lavishly washed with water and a strong solution of chromic acid. The gas then passed an adding gasometer and several drying columns, containing granulated calcium chloride and silica gel. The outlet from the reaction vessel was connected with a flask, containing calcium chloride and an empty inversed washing bottle, from which a tube led down into a cylinder, containing water. By raising and lowering the water level the pressure in the reaction bottle could be changed. An excess of pressure of 10 cm water column was usually used. By means of the water level it was possible to control whether the acetylene was completely absorbed or not in the reaction vessel.

As it had proved convenient to separate the vinyl acetate from inorganic compounds rapidly and at the lowest possible temperature, the reaction liquid was submitted to a simple distillation at reduced pressure. At the beginning of the distillation the pressure was 100—150 mm Hg and at the end 10—20 mm in order to obtain the most complete evaporation of ethylidene diacetate and other high-boiling compounds. The distillate was condensed in 2 or 3 stores, cooled to —10 or —20° C. The mixed distillates were then fractioned in a 120 cm column, fitted with reflux condensor.

The reaction mixture was usually prepared in a flask and then brought down into the reaction vessel. The quantities of the various components are shown in Table 1. Acetic anhydride is added in order to effect chemical binding of the water in the reaction mixture, as this is very important for the development of the complex catalyst acid and for the progress of the reaction.

According to the equation:

$$(CH_3 \cdot CO)_2O + H_2O \rightarrow 2\,CH_3COOH$$

Table 1.

	Experiment No.									
	1	2	3	4	5	6	7	8	9	10
Acetic acid . . . . . g	1 000	1 000	1 000	1 037	1 000	1 000	1 000	1 000	1 000	1 026
Acetic anhydride . . . . . »	167	212	250	100	0	105	92	90	150	200
Arsenic acid . . . . . »	—	—	6	6	6	6	4.5	4.5	3	3
Boric acid . . . . . »	5.3	—	—	—	—	—	—	—	—	—
Phosphorus penthoxide . . . . . »	—	5	—	—	—	—	—	—	—	—
Hydrogen fluoride acid (40 per cent) . . »	25	25	20	21	20	20	15	15	9	6
Mercury oxide . . . . . »	6	10	2.8	2.8	2.8	2.8	2.8	2.8	2.8	4
Acetylene . . . . . »	327	200	380	292	287	240	406	217	235	389
Sodium acetate . . . . . »	20	50	15	8	8	10	6	6	5	5
Reaction temperature . . . . . *circa* °C	17	37	18	20	16	10	15	15	15	15
Time of reaction . . . . . hours	7.5	6.5	7	5	6	2.5	6.5	4.5	8	8
Acetylene absorption at the end of the experiment . . . . . [1]	—	—	++	++	+	++	+	++	++	+
Vinyl acetate . . . . . g	920	555	1 069	783	427	700	965	625	685	1 053
Acetic acid . . . . . »	312	677	250	393	365	530	137	554	561	248
Ethylidene diacetate . . . . . »	79	105	360	186	210	87	247	80	105	239
Vinyl acetate yield calculated on converted C_2H_2 . . . . . per cent	85	84	85	81	45	88	72	87	88	82

[1] + = decreasing absorption; ++ = unchanged absorption.

5.7 g anhydride is consumed pr 1 g water. Probably the arsenic and the hydrogen fluoride acids in the presence of water will form a hydroxy acid with a rather low catalytic effect, which at complete removal of the water will be dehydrated or transformed into an acid of higher fluor content, which is more active. Removal of the water etc. is promoted by heating the reaction mixture to 40—60° C.

During the acetylene absorption the temperature was usually kept at 15—20° C by effective cooling. The previously light solution gradually darkened. Sometimes the colour might be very dark at the end of the reaction and the solution rather viscous, indicating the formation of tarry resins. At the end of the inlet of acetylene the solution was agitated for 10—15 min. for complete conversion of the remaining acetylene. Dry sodium acetate was then added in order to neutralize the strong complex acid, and agitation was continued for another 15—30 min. There was a considerable loss of vinyl acetate on vacuum distillation in spite of the cooling of the stores. This loss, however, has been determined and the yields accordingly corrected. On fractionation the first distillate was separated to 71° C, vinyl acetate between 71 and 75° C, a mixed distillate to 115° C and finally acetic acid between 115 and 120° C. In a few experiments the distillation was continued up to higher temperatures. In Table 1 all the products boiling over 120° C have however been named ethylidene diacetate, which is not quite accurate, since as well acetic acid as acetic anhydride (from the quantity charged) may be present. On the other hand part of the ethylidene diacetate might remain in the salt residue, obtained by the vacuum distillation. The quantities in the table give however a clear picture of the reaction progress.

On charging 1 kg acetic acid the first distillate usually held 10—30 g and the mixed distillate 15—30 g. Special investigations have shown that the quantities of acetaldehyde formed during the reaction do not exceed 1 or 2 per cent of the weight of the vinyl acetate and that the first distillate, received by the rectification, mainly consists of vinyl acetate. On calculating the yields the first distillate and the loss of the vacuum distillate have been considered as vinyl acetate.

On the other hand the vinyl acetate content of the mixed distillate, 75—115° C, has not been included.

The consequence of working with an absolutely water free solution was proved by a few experiments with boron acid according to the Swedish patent 86 490, ex. 3. It is true that acetylene was absorbed quite rapidly by use of 98—99 per cent acetic acid and 40 per cent hydrogen fluoride acid, but the vinyl acetate yield was low, and a large quantity of ethylidene diacetate and tarry substances were formed. However, on removing the water from the reaction mixture with acetic anhydride, a good yield of vinyl acetate (85 per cent) was obtained, as is shown in Table 1, in which the reacting quantities, given in the example of the patent, are approximately used.

To form the oxygen-free complex acid, $H[BF_4]$, 0.85 g HF (3.23 g 40 per cent acid) is required pr 1 g H_3BO_3 and for the complete neutralization 1.75 g HgO. According to ex. 3 and the first experiment hydrogen fluoride acid is used in a considerable excess, while the mercury oxide charged is hardly more than half the quantity needed for neutralization.

In the second experiment phosphorus anhydride is used to form the complex acid. The quantity of the catalyst was very large, but in spite of that the conversion had to take place at 35—40° C in order to obtain a good absorption of acetylene. In an experiment, not mentioned above, 5 g 80 per cent phosphoric acid, 20 g 40 per cent hydrogen fluoride acid, 3 g mercury oxide and a sufficient quantity of acetic anhydride were charged, and the solution heated to 50—60° C for 30 min. After cooling to 20° C acetylene was not absorbed. A considerable quantity evaporated, indicating that a satisfactory formation of complex acid had not occurred. According to the scant literature available the complex fluophosphoric acids seem to be less stable than those of boron and arsene.

With arsenic acid, however, very good results have been obtained, as Experiments 3—10 show. On account of the solubility of the arsenic acid as well as that of boron acid with fluoride acid, the catalyst may be prepared directly in the reaction mixture.

To form the oxygen-free complex acid, $H[AsF_6]$, 0.85 g HF (2.22 g 40 per cent acid) is required pr g H_3AsO_4 and to neutralize the acid 0.76 g HgO. In the experiments the quantities of the components mentioned have been varied within quite wide limits. In Experiments 9 and 10, for example, more mercury oxide has been used than required for the neutralization of the complex acid, whereas in the other experiments the mercury oxide was used in less than the theoretical quantity. In all the experiments but No. 10 an excess of hydrogen fluoride acid was added, as against the quantity required to form the oxygen free complex acid with no special influence on the vinyl acetate yield. According to Experiment 5 water in the reaction mixture affects adversely the vinyl acetate yield.

Part of the experiments in which the converted quantity of acetylene is low have been interrupted, before the decrease of the absorption. Where there is a high degree of conversion, the absorption has more or less completely stopped on account of the reduction of the mercury compound. A better vinyl acetate yield is usually obtained, if the experiment is broken off while plenty of acetic acid is still present in the solution.

According to our experiments arsenic acid seems to be noticeably more catalytically active than boric acid, and the relation between the components that constitute the catalyst changeable within wider limits, which may depend on the stability and degree of acidity of the complex acids. The antimone complex acids are more difficult to synthetisize in the reaction mixture owing to the low solubility of antimone acid and its oxide. A few experiments, however, seem to show that even antimone is able to form complex, active acids, but that working with arsenic acid is more convenient.

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Thiobenzoylaminosäuren.

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Übersicht.

Als Fortsetzung einer Untersuchung über die Verwendbarkeit der Thiobenzoylthioglykolsäure zur Darstellung von Thiobenzamiden (1) wurde diese Säure in neutralen Lösungen mit einigen Aminosäuren umgesetzt. In besonders einfacher Weise wurden hierbei gemäss der Gleichung (1):

$$C_6H_5CS \cdot SCH_2COONa + H_2NCH_2COONa = C_6H_5CS \cdot NHCH_2COONa + HSCH_2COONa \quad (1)$$

sowohl das Thiobenzoylglykokoll (Schmp. 150°—151°)[1] und der entsprechende Äthylester (Schmp. 51°—52°) wie das d,l-Thiobenzoylalanin (Schmp. 124°—125°) und die l-Form dieser Säure (bis jetzt nur als dickflüssiges Öl erhalten), die l-Thiobenzoylasparaginsäure und das l-Thiobenzoylasparagin (beide ölförmig), die l-Thiobenzoylglutaminsäure (kristallisiert mit 1 H_2O, Schmp. der wasserfreien Säure 111°—112°), die Thiobenzoylanthranilsäure (Schmp. 133°—134°) und die Thiobenzoylsulfanilsäure (als Na-Salz) sowie das Thiobenzoylsulfanilamid (Schmp. 244°—246°) gewonnen.

Bei Erhitzung des Thiobenzoylglykokolls in sauren oder neutralen Lösungen trat nur langsame Zersetzung ein, während es in alkalischer Lösung schnell und in zwei verschiedenen Richtungen zerfiel, nämlich gemäss der Gleichung (2) in Schwefelwasserstoff und Hippursäure:

$$C_6H_5CS \cdot NHCH_2COONa + NaOH = NaSH + C_6H_5CO \cdot NHCH_2COONa, \quad (2$$

[1] Alle Schmelzpunkte sind unkorrigiert.

und gemäss (3) in Thiobenzoesäure und Glykokoll:

$$C_6H_5CS \cdot NHCH_2COONa + NaOH = C_6H_5COSNa + H_2NCH_2COONa. \quad (3)$$

Eine bessere Methode zur Überführung der Thiobenzoyl- in Benzoyl-aminosäuren besteht in der Oxydation jener Säuren mit Wasserstoffsuperoxyd, wobei der Schwefel in freier Form oder als Schwefelsäure eliminiert und durch Sauerstoff ersetzt wird. Als die optisch aktiven Thiobenzoylaminosäuren dieser Reaktion unterworfen wurden, entstanden, ähnlich wie gemäss Fischer (2)[1] bei der direkten Benzoylierung der l-Glutaminsäure, etwas racemische Produkte und es ist daher fraglich, in welchem Grade auch die als nächste Ausgangsmaterialien verwendeten, aktiven Thiobenzoylaminosäuren und das hier zum ersten Mal in stöchiometrisch reiner Form gewonnene Benzoylasparagin sterisch einheitlich gewesen sind.

Für analytische Mithilfe bei dieser Untersuchung hat der Verfasser besonders Hrn Cand. real. Alf Tananger zu danken.

Beschreibung der Versuche.

1. *Thiobenzoylglykokoll.*

Eine Lösung von 4 g Natriumhydroxyd in 50 ml Wasser wurde mit 3,8 g Glykokoll und 10,6 g Thiobenzoylthioglykolsäure versetzt, wobei eine klare, rote Lösung entstand. Am folgenden Tage wurde die dann gelbe und auch nach der Filtrierung opalescente Lösung mit 25 ml 5-n. Salzsäure angesäuert, wobei ein Öl ausgeschieden wurde, welches nach Anreibung in 8,8 g einer grobkristallinischen Masse vom Schmp. 147°—148° (nach Verfärbung und unter Aufschäumen) und Äquiv.-Gew. 195,1 überging. Bei der Umkristallisierung aus einem Gemisch von 25 ml Sprit und 100 ml Wasser wurden 7,5 g lange, flache, gelbliche Prismen erhalten, welche unter Zersetzung wie oben bei 150°—151° schmolzen, in Alkohol und Azeton leicht, in Essigester und Äther ziemlich leicht und in Wasser und Benzol schwer löslich waren.

0,0899 g Sbst.: 0,1824 g CO_2 und 0,0369 g H_2O. — 0,2033 g Sbst.: 12,41 ml N_2 bei 21° und 760 mm. — 0,1752 g Sbst.: 0,2080 g $BaSO_4$. — 0,2127 g Sbst.: 10,81 ml 0,1009-n. NaOH.

[1] Siehe auch bei Carter and Stevens (3).

Für $C_6H_5CS \cdot NHCH_2COOH = C_9H_9O_2NS$ (195,23):

ber.: C 55,37, H 4,65, N 7,18, S 16,42 %, Äquiv.-Gew. 195,2,
gef.: » 55,37, » 4,59, » 7,09, » 16,31 », » » 195,0.

Als 3,8 g Thiobenzoylglykokoll mit 100 ml 2-n. Salzsäure auf dem Wasserbade erhitzt wurden, entstand eine schwach opalescente, blassgelbe Lösung, welche nach 3 Stunden nur eine Spur einer klebrigen Masse abgeschieden hatte; aus der davon abdekantierten Lösung kristallisierten danach beim Erkalten 2,9 g fast unveränderte Säure vom Schmp. 149°—150° (unter Zersetzung) und Äquiv.-Gew. 194,9. — Bei der gleichen Behandlung von 3,8 g Säure mit 100 ml Wasser wurden beim Erkalten der schwach milchig gewordenen Lösung 3,15 g Kristalle vom Schmp. 150°—151° (Zersetzung) und Äquiv.-Gew. 194,8 zurückgewonnen, und als 3,8 g Säure in mit 20 ml 1-n. Natronlauge neutralisierter Lösung 2 Stunden erhitzt wurden, lieferte dann die dabei unveränderte Lösung beim Ansäuern 3,7 g Kristallpulver vom Schmp. 149°—150° (Zersetzung) und Äquiv.-Gew. 195,2. — Beim Erhitzen in der gleichen Weise von einer aus 3,8 g Säure und 40 ml 1-n. Natronlauge bereiteten Lösung trat auch keine sichtbare Veränderung ein, aber beim Zusatz von 15 ml 5-n. Salzsäure wurde Schwefelwasserstoff freigemacht und eine Emulsion erhalten, welche ein teilweise kristallisierendes Öl abschied. Beim Absaugen wurden 1,1 g Kristalle gewonnen, welche bei ca. 180°—185° schmolzen und das Äquiv.-Gew. 182,5 zeigten, und somit aus unreiner Hippursäure bestanden. Auch beim Umkristallisieren aus verdünntem Alkohol wurde die Säure nicht ganz rein, denn sie schmolz dann bei 183°—186°, zeigte das Äquiv.-Gew. 178,1 statt ber. 179,2 und enthielt 7,43 %, ber. 7,82 %, N. — Das ölförmige Reaktionsprodukt wurde mit 8 ml 1-n. Natronlauge neutralisiert; nach Zusatz der gleichen Menge Lauge und Eiskühlung wurden auch 1,1 g Bromessigsäure zugefügt. Am folgenden Tage wurde beim Ansäuern ein Öl ausgeschieden, welches nach Impfung mit kristallisierter Benzoylthioglykolsäure (1) in 1,2 g farblose Blättchen überging. Das Produkt schmolz bei ca. 100°—105° und zeigte das Äquiv.-Gew. 191,5 und lieferte beim Umkristallisieren aus Benzol reine Benzoylthioglykolsäure vom Schmp. 107°—108°, Äquiv.-Gew. ber. 196,2, gef. 196,2,

und S ber. 16,34 %, gef. 16,33 %. Aus der Bildung dieser Säure geht hervor, dass das ursprüngliche Öl aus Tiobenzoesäure bestand.

Als eine Lösung von 3,9 g Thiobenzoylglykokoll in 20 ml 1-n. Natronlauge mit 8 g Perhydrol versetzt wurde, trat Wärmeentwicklung und Emulgierung ein. Durch Kühlung mit kaltem Wasser wurde die Temperatur unter 60° gehalten und am folgenden Tage konnten 2,6 g einer zum grössten Teil kristallinischen Masse abgesaugt werden. Dieses Produkt hinterliess bei der Behandlung mit 3 g Soda in 30 ml Wasser 0,4 g eines hauptsächlich aus freiem Schwefel bestehenden Pulvers, während das Filtrat davon beim Ansäuern mit Salzsäure 1,9 g Hippursäure vom Schmp. 185°—187° und Äquiv.-Gew. 180,6 lieferte. Aus dem Filtrat von dem ursprünglichen Reaktionsprodukt wurden mit Salzsäure noch 1,1 g Hippursäure vom Schmp. 186°—188° und Äquiv.-Gew. 179,6 ausgefällt und das Filtrat davon ergab mit Chlorbaryum eine kräftige Fällung.

Um den Äthylester des Thiobenzoylglykokolls zu erhalten, wurden 7 g Glykokollester-hydrochlorid und 10,6 g Thiobenzoylthioglykolsäure zu einer Lösung von 4 g Natriumhydroxyd in 50 ml Wasser gesetzt, wobei eine klare, rote Lösung entstand. Unter schwacher Wärmeentwicklung emulgierte sich die Lösung und ein dickflüssiges Öl wurde abgeschieden, welches beim Anreiben in einen kompakten Kristallkuchen von 8 g Gewicht und Schmp. 50°—51° überging. Bei vorsichtiger Fällung mit Petroläther aus seiner Lösung in Benzol wurde der Ester als gelbliche, nadelförmige Prismen vom Schmp. 51°—52° erhalten.

0,0884 g Sbst.: 0,1918 g CO_2 und 0,0463 g H_2O. — 0,1994 g Sbst.: 10,83 ml N_2 bei 21° und 751 mm. — 0,1782 g Sbst.: 0,1865 g $BaSO_4$.

Für $C_6H_5CS \cdot NHCH_2COOC_2H_5 = C_{11}H_{13}O_2NS$ (223,28):

ber.: C 59,17, H 5,87, N 6,27, S 14,36 %,
gef.: » 59,21, » 5,86, » 6,23, » 14,37 ».

2. *Thiobenzoylalanine.*

Aus 4 g Natriumhydroxyd in 50 ml Wasser, 4,5 g d,l-Alanin und 10,6 g Thiobenzoylthioglykolsäure wurde eine klare, rote

Lösung erhalten, welche sich bis zum folgenden Tage schwach trübte und orangerot wurde. Die nach Filtrierung klare Lösung schied mit 25 ml 5-n. Salzsäure ein Öl aus, welches nach Impfung mit Kristallen von einem Vorversuch in 9,2 g einer aus in verschiedenen Weisen mit einander aggregierten, mikroskopischen Prismen bestehenden Kristallmasse überging. Dieses Rohprodukt schmolz bei 120°—123° und zeigte das Äquiv.-Gew. 202,5. Bei der Umkristallisierung von 8,9 g davon aus 50 ml Benzol wurden 8,1 g blassgelbe, schmale Blättchen oder flache Prismen vom Schmp. 124°—125° erhalten.

0,0748 g Sbst.: 0,1576 g CO_2 und 0,0358 g H_2O. — 0,1085 g Sbst.: 6,20 ml N_2 bei 20° und 769 mm. — 0,1510 g Sbst.: 0,1682 g $BaSO_4$. — 0,2476 g Sbst.: 11,54 ml 0,1025-n. NaOH.

Für $C_6H_5CS \cdot NHCH(CH_3)COOH = C_{10}H_{11}O_2NS$ (209,26):

ber.: C 57,39, H 5,30, N 6,69, S 15,32 %, Äquiv.-Gew. 209,3,
gef.: » 57,50, » 5,36, » 6,74, » 15,30 », » » 209,3.

Beim Oxydieren von 2,1 g d,l-Thiobenzoylalanin in 10 ml 1-n. Natronlauge mit 4 g Perhydrol wie bei dem Thiobenzoylglykokoll wurden 1,1 g eines Gemisches von Schwefel und d,l-Benzoylalanin ausgeschieden; aus dem Filtrat davon wurden beim Ansäuern mit 5 ml 5-n. Salzsäure 0,9 g derselben Alaninverbindung vom Schmp. 158°—161° und Äquiv.-Gew. 194,0 ausgefällt. Aus dem genannten Gemisch wurden wie in dem vorigen Paragraphen 0,5 g d,l-Benzoylalanin vom Schmp. 159°—161° und Äquiv.-Gew. 194,7 gewonnen. Die beiden Präparate wurden zusammen aus 10 ml Wasser umkristallisiert und ergaben dabei schmale, flache Prismen vom Schmp. 159°—161°.

0,0835 g Sbst.: 0,1901 g CO_2 und 0,0422 g H_2O. — 0,1443 g Sbst.: 8,98 ml N_2 bei 20° und 753 mm. — 0,2367 g Sbst.: 12,16 ml 0,1005-n. NaOH.

Für $C_6H_5CO \cdot NHCH(CH_3)COOH = C_{10}H_{11}O_3N$ (193,20):

ber.: C 62,16, H 5,74, N 7,25 %, Äquiv.-Gew. 193,2,
gef.: » 62,13, » 5,66, » 7,18 », » » 193,7.

Nach Umsetzung von 4,5 g l-Alanin wie oben mit Thiobenzoylthioglykolsäure schied die Salzsäure 11,5 g eines dickflüssigen Öls aus, welches nicht zum Kristallisieren gebracht

werden konnte. Nach Neutralisierung des Öls mit 42,5 ml 1-n. Natronlauge wurden 30 ml der neutralen Lösung wie gewöhnlich mit 8 g Perhydrol oxydiert. Hierbei wurde nur Schwefel ausgeschieden und das Filtrat davon lieferte beim Ansäuern mit 10 ml 5-n. Salzsäure 2 g farblose, flache Prismen vom Schmp. 137°—139° und Äquiv.-Gew. 193,8. Beim Umkristallisieren von 1,7 g davon aus 17 ml Wasser wurden 1,25 g dünne Täfelchen von Schmp. wie vorher und Äquiv.-Gew. 193,3, ber. 193,2, erhalten.

1,015 g der umkristallisierten Säure wurden mit 5,25 ml 1,00-n. Natronlauge neutralisiert und die Lösung mit Wasser zu 10,04 ml verdünnt, wonach sie $\alpha_D^{20} = +3°,45$, $[\alpha]_D^{20} = +34°,1$ zeigte. — Gemäss Fischer[2] schmilzt das reine l(+)-Benzoylalanin bei 147°—148° und zeigt als K-Salz bei der gleichen Konzentration wie hier $[\alpha]_D^{20} = +37°,1$.

3. *l-Thiobenzoylasparaginsäure und l-Thiobenzoylasparagin.*

Eine aus 6 g Natriumhydroxid, 6,7 g l-Asparaginsäure und 10,6 g Thiobenzoylthioglykolsäure bereitete, klare und rote Lösung war am folgenden Tage gelbrot und hatte danach eine Spur eines schlammartigen Pulvers ausgeschieden. Das Filtrat war klar und ergab mit 35 ml 5-n. Salzsäure ein dickflüssiges Öl, welches nicht zum Kristallisieren gebracht werden konnte. Es wog 11,5 g und verbrauchte zur Neutralisierung 47 ml 1-n. Natronlauge. Die neutrale Lösung war etwas emulgiert und setzte bis zum folgenden Tage ein wenig Pulver ab. Von dem Filtrat nebst Waschwasser wurde eine 40 ml 1-n. Lauge entsprechende Menge (56 ml) wie üblich mit 8 g Perhydrol oxydiert, wonach am folgenden Tage das Filtrat von ausgeschiedenem Schwefel mit 10 ml 5-n. Salzsäure 3,3 g einer Benzoylasparaginsäure lieferte, welche bei 163°—164° schmolz und das Äquiv.-Gew. 120,9 zeigte. Beim Umkristallisieren von 3,0 g aus 50 ml mit etwas Tierkohle versetztem Wasser wurden 2,3 g mikroskopische, flache Prismen vom Schmp. 171°—173° erhalten.

0,0833 g Sbst.: 0,1696 g CO_2 und 0,0346 g H_2O. — 0,1268 g Sbst.: 6,55 ml N_2 bei 20° und 751 mm. — 0,1962 g Sbst.: 16,36 ml 0,1005-n. NaOH.

Für $C_6H_5CO \cdot NHCH(COOH)CH_2COOH = C_{11}H_{11}O_5N$ (237,21):

ber.: C 55,69, H 4,67, N 5,91 %, Äquiv.-Gew. 118,6,
gef.: » 55,56, » 4,65, » 5,95 », » » 119,3.

0,910 g Säure mit 7,67 ml 1,00-n. Natronlauge und Wasser zu 10,04 ml gelöst zeigten $\alpha_D^{20} = +3°,35$, $[\alpha]_D^{20} = +37°,0$. — Für reine l-Benzoylasparaginsäure fand Fischer (2) den Schmp. 180°—181° und für sie als K-salz bei der gleichen Konzentration wie hier $[\alpha]_D^{20} = +37°,4$.

Eine aus 4 g Natriumhydroxyd, 50 ml Wasser, 6,7 g l-Asparagin und 10,6 g Thiobenzoylthioglykolsäure bereitete, klare und rote Lösung war am folgenden Tage gelbrot und auch nach dem Filtrieren etwas opalescent. Nach Zusatz von 25 ml 5-n. Salzsäure wurde ein visköses, nicht kristallisierbares Öl ausgeschieden, welches 12,6 g wog und von 47 ml 1-n. Natronlauge neutralisiert wurde. Beim Stehen schied die Lösung eine unbedeutende Menge eines graulichen Pulvers aus; von der davon abfiltrierten, klaren Lösung nebst Waschwasser (70 ml) wurden 30 ml wie oben mit 8 g Perhydrol oxydiert. Dabei entstand ein Brei von Schwefel und feinkristallinischem Pulver, welcher nach Absaugen und Waschen mit Wasser mit 3 g Soda in 25 ml Wasser behandelt wurde. Das Filtrat von ungelöstem Schwefel lieferte beim Ansäuern 2 g eines äusserst feinkristallinischen Pulvers und aus dem Filtrat von der ursprünglichen Reaktionsmasse wurden in der gleichen Weise noch 0,4 g ähnlichen Pulvers gewonnen. Bei Umkristallisierung dieses rohen Benzoylasparagins aus der hundertfachen Menge Wasser wurden sternartig aggregierte, mikroskopische, nadelförmige Prismen vom Schmp. 189°—190° (unter Gasentwicklung) erhalten.

0,0758 g Sbst.: 0,1560 g CO_2 und 0,0348 g H_2O. — 0,1094 g Sbst.: 11,10 ml N_2 bei 18°,5 und 753 mm. — 0,2640 g Sbst.: 11,15 ml 0,1005-n. NaOH.

Für $C_6H_5CO \cdot NHCH(COOH)CH_2CONH_2 = C_{11}H_{12}O_4N_2$ (236,22):

ber.: C 55,93, H 5,12, N 11,86 %, Äquiv.-Gew. 236,2,
gef.: » 56,16, » 5,14, » 11,77 », » » 235,6.

Eine Lösung von 1,057 g Sbst. in 4,48 ml 1,00-n. Natronlauge und Wasser zu 10,04 ml zeigte $\alpha_D^{20} = +1°,99$, $[\alpha]_D^{20} = +18°,9$.

Bei der direkten Benzoylierung von l-Asparagin erhielten Pauly und Weir (4) ein Benzoylasparagin vom Schmp. 190°—196°, welches sie von anhaftender Benzoylasparaginsäure nicht vollständig befreien konnten; beim Umsatz von Benzoylasparaginsäureanhydrid mit wässerigem Ammoniak gewannen sie eine Benzoylasparaginamidsäure vom Schmp. 211°—212°. Die Stellung der Amidgruppe in dieser Säure wurde jedoch nicht ermittelt und für keines der Produkte wurde das Drehungsvermögen bestimmt.

4. *l-Thiobenzoylglutaminsäure.*

Aus 6 g Natriumhydroxyd, 7,4 g l-Glutaminsäure und 10,6 g Thiobenzoylthioglykolsäure wurde eine klare, rote Lösung erhalten. Am folgenden Tage war das Gemisch rotgelb und auch nach Filtrierung schwach milchig; mit 25 ml 5-n. Salzsäure lieferte es dann eine Emulsion, welche allmählich ein dickflüssiges Öl abschied. Als eine Probe davon auf dem Uhrglas angerieben wurde, fing sie zum Schluss an zu kristallisieren und nach Impfung damit ging die Hauptportion des Öles im Eisschrank in 9,8 g einer grobkristallinischen Masse über, welche bei ca. 60°—90° schmolz und das Äquiv.-Gew. 145,1 zeigte. Dieses Rohprodukt wurde in Essigester gelöst und die Lösung mit Benzol versetzt, bis Emulgierung einzutreten begann, wonach das Gemisch nach Impfung mit dem Rohprodukt und im Eisschrank eine Kruste von gelblichen Prismen, 6,5 g, ausschied. Im zugeschmolzenen Röhrchen schmolz das Produkt bei 68°—70°, und nach Entwässerung zeigte es den Schmp. 111°—112°.

0,3701 g Sbst.: im Vakuum über P_2O_5 0,0233 g Gewichtsverlust. — 0,0895 g Sbst.: 0,1658 g CO_2 und 0,0417 g H_2O. — 0,1316 g Sbst.: 5,71 ml N_2 bei 17° und 747 mm. — 0,2022 g Sbst.: 0,1640 g $BaSO_4$. — 0,1541 g Sbst.: 10,72 ml 0,1005-n. NaOH.

Für $C_6H_5CS \cdot NHCH(COOH)CH_2CH_2COOH$, H_2O = $= C_{12}H_{15}O_5NS$ (285,31):

ber.: H_2O 6,31, C 50,51, H 5,30, N 4,91, S 11,24 %, Äquiv.-Gew. 142,7,
gef.: » 6,30, » 50,55, » 5,21, » 5,02, » 11,14 », » » 143,0.

0,500 g Sbst. in abs. Alkohol zu 10,04 ml: $\alpha_D^{20} = +2°,27$, $[\alpha]_D^{20} = +45°,6$, $[M]_D^{20} = +130°,0$. — 1,010 g mit 7,08 ml 1,00-n. Natronlauge und Wasser zu 10,04 ml: $\alpha_D^{20} = +3°,08$, $[\alpha]_D^{20} = +30°,6$ und $[M]_D^{20} = +87°,4$.

Aus der Mutterlauge dieses Präparates wurden nach Zusatz von mehr Benzol noch 1,7 g Kristalle erhalten, welche im zugeschmolzenen Röhrchen bei 68°—69° schmolzen und das Äquiv.-Gew. 143,0 zeigten. — 0,5175 g in abs. Alkohol zu 10,04 ml gelöst zeigten $\alpha_D^{20} = +2°,22$, $[\alpha]_D^{20} = +43°,1$.

Bei der Oxydation von 5,7 g der ersten, umkristallisierten Fraktion in 40 ml 1-n. Natronlauge mit 8 g Perhydrol wie bei den anderen Säuren wurde nur etwas Schwefel abgeschieden; als das Filtrat davon mit 10 ml 5-n. Salzsäure versetzt wurde, trat nur eine schwache Opalescierung ein. Nach Zusatz von etwas Tierkohle und Filtrierung ergab die Lösung allmählich im Eisschrank 0,7 g farblose, flache Prismen oder dünne Täfelchen, welche aus fast inaktiver Benzoylglutaminsäure bestanden. Im zugeschmolzenen Röhrchen schmolz das Produkt bei ca. 95° zu einer halbflüssigen Masse und zeigte nach Entwässerung den Schmp. 152°—155°. Sein Äquiv.-Gew. betrug 135,6, mit 1 H_2O ber. 134,6, und eine Lösung von 0,505 g in 3,75 ml 1,00-n. Natronlauge und Wasser zu 10,04 ml zeigte $\alpha_D^{20} = +0°,10$. Bei der freiwilligen Eindunstung der mit Salzsäure versetzten, polarisierten Lösung wurden flache Prismen erhalten, welche im Vakuum über Phosphorsäureanhydrid 6,56 %, ber. 6,69 %, an Gewicht verloren, in trockener Form bei 154°—156° schmolzen und bei der Analyse ergaben:

0,0836 g Sbst.: 0,1762 g CO_2 und 0,0388 g H_2O. — 0,1183 g Sbst.: 5,45 ml N_2 bei 19° und 765 mm.

Für $C_6H_5CO \cdot NHCH(COOH)CH_2CH_2COOH = C_{12}H_{13}O_5N$ (251,23):

ber.: C 57,37, H 5,22, N 5,58 %,
gef.: » 57,52, » 5,19, » 5,42 ».

Bei der freiwilligen Eindunstung der Mutterlauge nach der zuerst abgeschiedenen, fast inaktiven Benzoylglutaminsäure wurden noch 2,7 g Kristalle erhalten, welche im Vakuum über Phosphorsäureanhydrid 0,77 % an Gewicht verloren, dann bei 126°—128° schmolzen und bei der Analyse ergaben:

0,1056 g Sbst.: 0,2221 g CO_2 und 0,0492 g H_2O. — 0,1314 g Sbst.: 6,60 ml N_2 bei 18° und 732 mm. — 0,1552 g Sbst.: 12,26 ml 0,1005-n. NaOH.

Für $C_6H_5CO \cdot NHCH(COOH)CH_2CH_2COOH = C_{12}H_{13}O_5N$ (251,23):

ber.: C 57,37, H 5,22, N 5,58 %, Äquiv.-Gew. 125,6,
gef.: » 57,40, » 5,21, » 5,67 », » » 126,0.

0,489 g Sbst. in Wasser zu 10,04 ml: $\alpha_D^{20} = -0°,56$, $[\alpha]_D^{20} = -11°,5$. — 1,000 g Sbst. mit 7,96 ml 1,00-n. Natronlauge und Wasser zu 10,04 ml: $\alpha_D^{20} = +1°,87$, $[\alpha]_D^{20} = +18°,7$.

Für die wasserfreie d, l-Benzoylglutaminsäure gibt Fischer (2) den Schmp. 152°—154° und für die reine d-Säure 128°—130° an. Für diese Säure fand er $[\alpha]_D^{20} = +13°,8$ (0,5 g in 10 ml Wasser), bzw. $= -18°,7$ (für 1,1 g als K-Salz in 10 ml Wasser).

5. *Thiobenzoylanthranilsäure.*

Aus 1,8 g Natriumhydroxyd, 25 ml Wasser, 3,1 g Anthranilsäure und 5,0 g Thiobenzoylthioglykolsäure wurde eine rote Lösung erhalten, welche sich bis zum folgenden Tage nicht sichtbar veränderte. Als sie dann unter Impfung mit Kristallen von einem Vorversuch und in mehreren Portionen mit 10 ml 5-n. Salzsäure versetzt wurde, entstand ein Brei eines rotgelben, grobkristallinischen Pulvers, 5,7 g, welches beim Umkristallisieren aus 25 ml Sprit 3,5 g gelbe, flache, wetzsteinartig zugespitzte Prismen vom Schmp. 133°—134° (unter Gasentwicklung) lieferte.

0,0797 g Sbst.: 0,1902 g CO_2 und 0,0304 g H_2O. — 0,1407 g Sbst.: 6,80 ml N_2 bei 20° und 753 mm. — 0,1599 g Sbst.: 0,1458 g $BaSO_4$. — 0,3011 g Sbst.: 11,70 ml 0,1005-n. NaOH.

Für $C_6H_5CS \cdot NHC_6H_4COOH = C_{14}H_{11}O_2NS$ (257,30):

ber.: C 65,35, H 4,31, N 5,44, S 12,46 %, Äquiv.-Gew. 257,3,
gef.: » 65,12, » 4,27, » 5,58, » 12,52 », » » 256,1.

Bei der Oxydation von 5,1 g Thiobenzoylanthranilsäure in 40 ml 1-n. Natronlauge mit 8 g Perhydrol trat sogleich eine so starke Wärmeentwicklung ein, dass die Temperatur trotz unmittelbarer Kühlung mit kaltem Wasser auf 90° stieg. Beim

Erkalten entstand ein Brei aus ausgeschiedenem Schwefel und nadelförmigen Kristallen des Natriumsalzes der Benzoylanthranilsäure. Beim Erwärmen mit 50 ml Wasser ging das Salz in Lösung, um sich beim Erkalten nur in unbedeutender Menge wieder abzuscheiden; das Filtrat davon lieferte beim Ansäuern eine teigige, bald kristallinisch erstarrende Masse vom Schmp. 176°—178° und Äquiv.-Gew. 243,8. Beim Umkristallisieren aus Sprit wurde die so gewonnene Benzoylanthranilsäure als flache, fast nadelförmige Prismen vom Schmp. 177°—178° (gemäss den Angaben in Beilstein 177°, 178°, 179°—181° oder 182°), Äquiv.-Gew. 243,7, ber. 241,2, und N = 5,71 %, ber. 5,81 %, erhalten.

6. *Thiobenzoylsulfanilsäure und Thiobenzoylsulfanilamid.*

Eine klare, rote Lösung von 4 g Natriumhydroxyd, 8,7 g Sulfanilsäure und 10,6 g Thiobenzoylthioglykolsäure in 50 ml Wasser begann nach einigen Stunden gelbe, dünne Blätter abzuscheiden und war am folgenden Tage breiartig erstarrt. Nach Absaugen und Waschen der fast neutral reagierenden, in heissem Wasser zu einer etwas milchigen Lösung löslichen Blätter wurde das Filtrat erwärmt und mit 20 ml 5-n. Salzsäure versetzt. Dabei entstand eine Emulsion, welche 0,9 g rote Schuppen absetzte. Diese schmolzen bei 122°—125° und bestanden somit aus unverbrauchter Thiobenzoylthioglykolsäure. Die Mutterlauge lieferte bei der freiwilligen Eindunstung auch gelbe Blätter, welche zusammen mit den wiedergewonnenen, zuerst ausgeschiedenen aus verdünntem Alkohol umkristallisiert wurden und dann die Zusammensetzung des Natriumsalzes der Thiobenzoylsulfanilsäure zeigten.

0,1289 g Sbst.: 5,02 ml N_2 bei 17° und 763 mm. — 0,1904 g Sbst.: 0,2776 g $BaSO_4$. — 0,3208 g Sbst.: 0,0710 g Na_2SO_4.

Für $C_6H_5CS \cdot NHC_6H_4SO_3Na = C_{13}H_{10}O_3NS_2Na$ (315,33):

ber.: N 4,44, S 20,33, Na 7,29 %,
gef.: » 4,60, » 20,03, » 7,17 ».

Als eine Lösung von 8,4 g Thiobenzoylthioglykolsäure in 40 ml 1-n. Natronlauge mit 6,8 g Sulfanilamid erwärmt wurde, entstand eine klare Lösung, welche bald zu einem gelben Brei

von mikroskopischen, zu Bällen vereinigten, nadelförmigen Prismen überging. Nach einer halben Stunde auf dem Wasserbade und Erkalten konnten 9,8 g rohes Thiobenzoylsulfanilamid vom Schmp. 243°—245° abgenutscht werden und nach Umkristallisieren durch vorsichtige Fällung mit Wasser aus seiner Lösung in warmem Azeton schmolz das dabei als gelbe Nädelchen erhaltene Amid bei 244°—246°.

0,0949 g Sbst.: 0,1857 g CO_2 und 0,0348 g H_2O. — 0,1314 g Sbst.: 10,65 ml N_2 bei 20° und 758 mm. — 0,1721 g Sbst.: 0,2717 g $BaSO_4$.

Für $C_6H_5CS \cdot NHC_6H_4SO_2NH_2 = C_{13}H_{12}O_2N_2S_2$ (292,36):

ber.: C 53,40, H 4,14, N 9,58, S 21,93 %,

gef.: » 53,40, » 4,10, » 9,42, » 21,68 ».

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Zur Kenntnis der Komplexbildung zwischen Silber und einigen schwefelhaltigen Karbonsäureionen in wässeriger Lösung.

Von Erik Larsson.

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1. Im folgenden werden einige Versuche erörtert, die ausgeführt wurden, um Kenntnis über die Komplexe zu erhalten, die in wässeriger Lösung zwischen Silber und einigen Karbonsäureionen mit C-S-C-Bindungen entstehen. Der Übersicht halber sind die untersuchten komplexbildenden Karbonsäureionen in drei Gruppen zusammengefasst:

erste Gruppe: die einwertigen Ionen der S-Äthyl-, S-Phenyl- und S-Benzyl-thioglykolsäuren sowie der S-Benzyl-β-merkaptopropionsäure,

zweite Gruppe: die zweiwertigen Ionen der Thiodiessigsäure, der β-Thiodipropionsäure und der γ-Thiodibuttersäure,

dritte Gruppe: die zweiwertigen Ionen der Polymethylenbisthioglykolsäuren

$$HOCO \cdot CH_2 \cdot S \cdot (CH_2)_n \cdot S \cdot CH_2 \cdot COOH$$

mit $n = 1—6$.

2. Lösungen mit bekannten Konzentrationen von Silbernitrat und dem neutralen Natriumsalz der betreffenden schwefelhaltigen Säure wurden hergestellt und die Silberionenkonzentrationen mittels einer Silberelektrode bei 20°,0 gemessen. Um den gemessenen Lösungen bestimmte Kationenkonzentrationen zu geben, wurde Natriumnitrat zugesetzt.

Bjerrum (1) und Leden (2) haben das allgemeine Problem der Berechnung von Dissoziations- und Beständigkeitskonstanten der Komplexe MA, MA_2, MA_3, . . . MA_n behandelt, wenn man die Konzentrationen des Liganden A oder des Ions M in einer

Reihe Lösungen mit bekannten Gesamtkonzentrationen von M und A kennt. Eine Durchrechnung meines Versuchsmaterials zeigte sofort, dass das Silber in den untersuchten Lösungen nur in der Form von Komplexen AgA and AgA_2 (A ist das Anion der komplexbildenden schwefelhaltigen Säure) und als freie Silberionen vorhanden sein kann. Weiter war es möglich, für jedes Ag-A-System Lösungen darzustellen, aus deren Silberionenkonzentrationen man das Produkt der Gleichgewichtskonstanten k_1 und k_2 der beiden Gleichgewichte

$$Ag^+ + A \rightleftarrows AgA \qquad (1)$$

$$AgA + A \rightleftarrows AgA_2 \qquad (2)$$

berechnen konnte, ohne die einzelnen Konstanten k_1 and k_2 zu kennen. Dies bedeutet, dass die rechnerische Behandlung der Messungen einfacher als in dem allgemeinen Falle wird.

3. Für eine Lösung mit den Gesamtkonzentrationen a und b des Silbers bzw. des komplexbildenden Karbonsäureions und mit den Komplexen AgA und AgA_2 gelten die folgenden Gleichungen:

$$[AgA] = k_1 \cdot [Ag^+]\,[A] \qquad (3)$$

$$[AgA_2] = k_2 \cdot [AgA]\,[A] \qquad (4)$$

$$a = [Ag^+] + [AgA] + [AgA_2] \qquad (5)$$

$$b = [A] + [AgA] + 2\,[AgA_2] \qquad (6)$$

Hier bedeuten k_1 und k_2 die Konzentrationsgleichgewichtskonstanten der Gleichgewichte (1) und (2) bei den Ionenkonzentration der Lösung. Es wird angenommen, dass die Nitrationen keine Komplexe mit Silber geben.

Aus den Gleichungen (3)—(6) findet man leicht:

$$[A] = \frac{b - 2a + 2\,[Ag^+]}{1 - k_1\,[Ag^+]} \qquad (7)$$

$$[AgA] = \frac{(b - 2a + 2\,[Ag^+])\,k_1\,[Ag^+]}{1 - k_1\,[Ag^+]} \qquad (8)$$

$$[AgA_2] = \frac{a - [Ag^+] - (b - a + [Ag^+])\,k_1\,[Ag^+]}{1 - k_1\,[Ag^+]} \qquad (9)$$

$$(b - a + [Ag^+])[Ag^+]^2 k_1^2 - b[Ag^+] k_1 - \\ - (b - 2a + 2[Ag^+])^2 K[Ag^+] + a - [Ag^+] = 0 \qquad (10)$$

oder

$$\{a - [Ag^+] - (b - 2a + 2[Ag^+])^2 K[Ag^+]\} k_2^2 - b K[Ag^+] k_2 + \\ + (b - a + [Ag^+]) K^2 [Ag^+]^2 = 0. \qquad (11)$$

In (10) und (11) ist K das Produkt $k_1 \cdot k_2$. Wenn man annehmen kann, dass das Silber praktisch nur als Silberion und als AgA_2 in der Lösung vorkommt, gilt:

$$K = \frac{a[Ag^+]}{(b - 2a + 2[Ag^+])^2 [Ag^+]}. \qquad (12)$$

Bei den im folgenden untersuchten Komplexsystemen ist es immer möglich Lösungen darzustellen, aus deren Silberionenkonzentrationen man K nach (12) berechnen kann. Dies trifft zu, wenn man das Verhältnis zwischen b und a hinreichend gross wählt. Die nach (12) errechneten K-Werte sind da von der Zusammensetzung der Lösung unabhängig. Die Silberionenkonzentrationen der Lösungen, für die (12) nicht gilt, können zur Berechnung von k_1 nach (10) oder k_2 nach (11) verwendet werden, wenn man K als bekannt voraussetzt. Von den beiden Wurzeln der Gleichungen (10) und (11) hat man diejenige zu wählen, die positive Werte für die Konzentrationen [A], [AgA] und $[AgA_2]$ gibt.

4. Die Tabelle 1 zeigt einige der Messungen an Natriumbenzylthioglykolat-Silbernitrat-Lösungen. Die Silberionenkonzentrationen sämtlicher Lösungen geben nach (12) innerhalb der Versuchsfehler übereinstimmende Werte für $\log K$. Die einzelnen Konstanten k_1 und k_2 können bei diesem Komplexsystem nicht bestimmt werden, weil Lösungen, die hierfür geeignet sind, wegen der Bildung schwerlöslicher Silberverbindungen, nicht hergestellt werden können. Die übrigen Anionen der ersten und zweiten Gruppe verhalten sich in derselben Weise wie das Benzylthioglykolation der Tabelle 1. Das Endresultat der Messungen und Berechnungen habe ich in den Tabellen 2 und 3 zusammengestellt. In keinem Fall war es möglich, k_1 und k_2 einzeln zu bestimmen. Man kann jedoch aus den Messungen schätzen, dass $k_1 < 10 \cdot k_2$ ist. Die Mes-

Tabelle 1. Natriumbenzylthioglykolat-Silbernitrat ($[Na^+] = 1{,}0$).

a	b	$-\log[Ag^+]$	$\log K$
0,0005	0,04	7,61	7,13
0,0005	0,02	6,99	7,13
0,0005	0,01	6,86	7,16
0,001	0,08	7,90	7,12
0,001	0,04	7,26	7,13
0,001	0,02	6,61	7,11
0,001	0,01	5,95	7,14
0,002	0,04	6,95	7,14
0,002	0,01	5,42	7,19
0,004	0,02	5,66	7,10
0,008	0,01	5,42	7.19
		Mittel	7,13

Tabelle 2. Log K der Komplexe mit den Anionen der ersten Gruppe.

$[Na^+]$ / Säureanion	0,04	0,25	0,5	1,0
	$\log K$	$\log K$	$\log K$	$\log K$
$C_2H_5 \cdot S \cdot CH_2 \cdot COO^-$	7,20	7,14	7,19	7,25
$C_6H_5 \cdot S \cdot CH_2 \cdot COO^-$	7,31	7,25	7,28	7,27
$C_6H_5 \cdot CH_2 \cdot S \cdot CH_2 \cdot COO^-$ . .	7,22	7,14	7,13	7,13
$C_6H_5 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot COO^-$	7,35	7,34	7,34	7,34

Tabelle 3. Log K der Komplexe mit den Anionen der zweiten Gruppe.

$[Na^+]$ / Säureanion	0,04	0,25	0,5	1,0
	$\log K$	$\log K$	$\log K$	$\log K$
$S(CH_2 \cdot COO^-)_2$	6,57	6,30	6,29	6,32
$S(CH_2 \cdot CH_2 \cdot COO^-)_2$	6,91	6,84	6,74	6,71
$S(CH_2 \cdot CH_2 \cdot CH_2 \cdot COO^-)_2$ . .	—	6,98	7,02	7,00

sungen wurden bei den Natriumionenkonzentrationen 0,04, 0,25, 0,5, und 1,0 ausgeführt.

5. Die Tabelle 4 zeigt einige Messungen an Natriumäthylenbisthioglykolat-Silbernitrat-Lösungen, aus deren Silberionenkonzentrationen man sowohl K wie k_1 (und damit auch k_2) berechnen kann. Die 10 Lösungen geben K nach der Formel (12) und die übrigen k_1 nach (10). In ähnlicher Weise verhalten sich alle andere Komplexe mit den Anionen der dritten Gruppe.

Die Tabelle 5 zeigt eine Zusammenstellung der Werte für $\log K$, $\log k_1$ und $\log k_2$ der Silberkomplexe mit den Anionen der dritten Gruppe. Die Konstanten wurden nur bei der Ionenkonzentration 1,0 ermittelt. Die $\log K$-Werte sind auf etwa 0,05 genau. Die $\log k_1$- und $\log k_2$-Werte haben eine Genauigkeit von nur etwa 0,1—0,2. Die in der Tabelle angegebenen Konstanten für das Silber-Methylenbisthioglykolatsystem erklären in grossen Zügen die Verhältnisse in dem System. Einige Anomalien wurden jedoch beobachtet, die möglicherweise darauf deuten, dass in diesem System auch andere (wahrscheinlich zweikernige) Komplexe als AgA und AgA_2 vorkommen können. Ihre Mengen dürften jedoch geringfügig sein.

6. Die Komplexe AgA sind neutrale Moleküle, wenn A zu den Anionen der ersten Gruppe gehört, sonst sind sie einwertige Anionen. Die Komplexe AgA_2 sind im ersteren Falle einwertige sonst dreiwertige Anionen.

Es ist schwierig auf Grund des vorliegenden Materiales, unangreifbare theoretische Erwägungen über die verschiedenen Komplexe anzustellen. Folgendes möchte ich jedoch sagen.

Wenn A nur ein Schwefelatom enthält, kann man annehmen, dass die Bindung zwischen A und Ag^+ durch „Nebenvalenzen" des Schwefels und des Silbers herbeigeführt wird und dass die A-Ionen in AgA und AgA_2 gleichwertig gebunden sind. Man hat da zu erwarten, dass k_1/k_2 aus statistischen Gründen gleich 4 ist. Dieses Verhältnis kann jedoch einen anderen Wert haben, weil Effekte eine Rolle spielen können, die schwer zu überblicken sind. Die Versuche haben gezeigt, dass k_1/k_2 kleiner als 10 ist. Die $\log K$-Werte der Tabellen 2 und 3 liegen alle bei 6,3—7,3. Die $\log K$-Werte der Komplexe mit den einwertigen Ionen sind etwas höher als diejenigen der Komplexe mit zweiwertigen Ionen. Unter den Letzten haben die Silber-

Tabelle 4. Natriumäthylenbisthioglykolat-Silbernitrat-Lösungen ($[Na^+] = 1{,}0$).

a	b	$-\log[Ag^+]$	$\log K$	$\log k_1$
0,001	0,04	10,57	10,41	
0,001	0,02	9,91	10,40	
0,001	0,01	9,22	10,42	
0,001	0,005	8,38	10,43	
0,001	0,004	8,05	10,45	
0,001	0,003	7,50	10,50	
0,004	0,04	9,81	10,40	
0,004	0,02	8,95	10,39	
0,004	0,01	7,60	(10,60)	
0,004	0,008	6,45		6,5
0,004	0,007	5,89		6,7
0,004	0,006	5,20		6,3
0,004	0,005	—[1]		
0,008	0,04	9,26	10,40	
0,01	0,06	9,60	10,40	
0,01	0,02	6,48		6,5
0,01	0,018	5,76		6,6
0,01	0,016	5,05		6,5
0,01	0,014	—[1]		

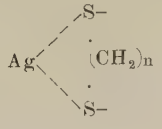
[1] Aus der Lösung fiel eine schwerlösliche Verbindung aus.

Tabelle 5. Log K, $\log k_1$ und $\log k_2$ der Komplexe mit den Anionen der dritten Gruppe ($[Na^+] = 1{,}0$).

Säureanion vom Typus $^-OCO \cdot CH_2 \cdot S \cdot (CH_2)_n \cdot S \cdot \cdot CH_2 \cdot COO^-$ mit n	$\log K$	$\log k_1$	$\log k_2$
1	6,50	4,7	1,8
2	10,41	6,5	3,9
3	8,09	5,7	2,4
4	8,36	6,0	2,3
5	8,85	6,3	2,6
6	8,55	6,0	2,6

Thiodiacetat-Komplexe einen kleineren Wert als die Silber-γ-Thiodibutyrat-Komplexe. Die Silber-β-Thiodipropinat-Komplexe liegen dazwischen. Der grössere Abstand zwischen dem Schwefelatom und der Karboxylgruppe macht die Komplexe stabiler

Die log K-Werte der Komplexe mit den Anionen der Säuren mit zwei Schwefelatomen (Tabelle 5) sind wesentlich höher als die log K-Werte der Komplexe mit nur einem Schwefelatom in A, wenn $n = 2$—6 ist. Dies deutet auf eine stärkere Bindung zwischen Silber und A. Interessant sind die log k_1-Werte. Diese sind für die Komplexe mit $n = 2$—6 5,7—6,5 und somit etwas kleiner als die log-K-Werte der AgA_2-Komplexe mit nur einem Schwefelatom in dem A-Ion. Dies macht es wahrscheinlich, dass die Bindung zwischen Silber und A in AgA durch „Nebenvalenzen" der *beiden* Schwefelatome in A vermittelt wird, wenn $n = 2$—6 ist. Das Silber-Methylenbisthioglykolat-Komplex hat einen kleineren log k_1-Wert als die anderen Komplexe der Gruppe. Die AgA-Komplexe mit Methylenbisthioglykolationen dürften daher zum Teil nur Nebenvalenzbindung zwischen Silber und dem *einen* Schwefelatom des A-ions haben. Diese Verschiedenheit in den Bindungsverhältnissen bei den Polymethylenbisthioglykolationen wird auch verständlich, wenn man an die Spannungsverhältnisse in dem Ring



denkt. Es ist leicht einen Ring mit geringer Spannung zu erhalten, wenn n hoch ist. Man darf nur nicht fordern, dass die verschiedenen Atome des Ringes in derselben Ebene liegen sollen.

Die Bindung des A-Ions an Silber in den AgA_2-Komplexen, wo A ein Polymethylenbisthioglykolation ist, dürfte nur von dem einen Schwefelatom in A vermittelt werden. Die A-Ionen in AgA und AgA_2 dürften da nicht in gleichwertiger Weise gebunden sein, wodurch die bei diesen Komplexen gefundenen grossen k_1/k_2-Verhältnisse erklärlich sind.

Beschreibung der Versuche.

7. Die Silberionenkonzentration einer Lösung mit a Mol Silbernitrat, b Mol NaA (wenn A einwertig ist) oder b Mol Na_2A (wenn A zweiwertig ist) und $c-a-b$ bzw. $c-a-2\,b$ Mol Natriumnitrat (c ist die Natriumionenkonzentration der Lösung) pr Liter wurde elektrometrisch bei 20°,0 mit Hilfe der Kette

$$\text{Ag} \;\Big|\; \text{Lösung} \;\Big|\; c-m\ \text{NaNO}_3 \;\Big|\; \begin{matrix} 0{,}01-m\ \text{AgNO}_3 \\ (c-0{,}01)-m\ \text{NaNO}_3 \end{matrix} \;\Big|\; \text{Ag}$$

gemessen. Aus der elektromotorischen Kraft E dieser Kette erhält man die Silberionenkonzentration nach der Formel:

$$-\log [\text{Ag}^+] = \frac{E - 0{,}0581 \log 0{,}01}{0{,}0581}. \qquad (13)$$

Die Versuchslösungen wurden mittels einer Lösung des Natriumsalzes NaA bzw. Na_2A, einer Silbernitratlösung und einer konzentrierten Natriumnitratlösung oder festem Natriumnitrat hergestellt. Die Natriumnitrat- und Silbernitratlösungen wurden aus analysenreinen Salzen, die Lösungen von NaA und Na_2A aus den freien Säuren und kohlensäurefreier Natronlauge in berechneten Mengen hergestellt. Die schwefelhaltigen Säuren wurden nach bekannten Methoden (3) dargestellt. Die Prüfung der Säuren auf ihre Reinheit erfolgte durch Bestimmungen der Schmelzpunkte und Äquivalentgewichte.

Als Silberelektroden wurden Elektroden verwendet, die aus nach Brown (4) hergestellten Silberchloridelektroden durch Auslösen des Silberchlorids mit Ammoniak erhalten wurden. Die Messungen in der Tabelle 6 sind mit solchen Elektroden ausgeführt. Es wurde die elektromotorischen Kräfte der Ketten

$$\text{Ag} \;\Big|\; \begin{matrix} (1-a)-m\ \text{NaNO}_3 \\ a-m\ \text{AgNO}_3 \end{matrix} \;\Big|\; 1-m\ \text{NaNO}_3 \;\Big|\; \text{Vergleichselektrode}$$

bei 20°,0 gemessen. Aus denselben wurde E_0 nach der Formel

$$E_0 = E - 0{,}0581 \log a \qquad (14)$$

errechnet. Die gute Konstanz der E_0-Werte zeigt, dass die Elektrodenpotentiale sich genau nach den Silberionenkonzentrationen der Lösungen einstellen.

Tabelle 6.

a	E	E_0
0,001	0,3667	0,5410
0,002	0,3851	0,5411
0,004	0,4022	0,5415
0,008	0,4194	0,5412
0,01	0,4250	0,5412
0,02	0,4428	0,5410
0,08	0,4528	0,5410
0,04	0,4602	0,5414
0,05	0,4657	0,5413

Die obige Untersuchung wurde im Jahre 1935 im Chemischen Institut der Universität Lund begonnen. Danach wurde sie vor allem in den Jahren 1943—1944 an der Chalmers Techn. Hochschule weitergeführt, wobei sie von „Chalmersska Forskningsfonden" unterstützt wurde. Die Untersuchung wird in verschiedenen Richtungen fortgesetzt.

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Wire Enamels.

By Halvard Liander.

From the Allmänna Svenska Elektriska Aktiebolaget, Västerås.

The insulation of copper wire has always been an important problem to the electric industry. For a long time the wire was covered with silk or cotton and then usually impregnated with some kind of insulating varnish. The advantages of using a thin homogeneous film instead of the silk or cotton yarn were, however, early recognised, and some 40 years ago enamelled wire was introduced in the manufacture of electrical apparatus. This meant reduced costs, improved electric properties and a better space factor, especially in the case of small wires.

Many kinds of materials had then been tried more or less with success, such as collodion, casein, albumen, glue, rubber and silk solution etc., but only drying oil-base enamels and cellulose acetate found commercial application (1). Later, cellulose acetate, which had been used extensively for small diameters (1, 2, 3) was abandoned in favour of enamels.

Enamelled wire gained an ever increasing importance. Having first been used only where the space factor was particularly important, e. g. in coils for meters, relays, and telephones, it soon found its way to small motors, shunts for d. c. machinery and transformer coils. A further development was the substitution of double cotton covered wire by enamelled wire with one layer of cotton for a. c. machinery (4). There has been some hesitation in taking the last step — to discard even the remaining layer of cotton or paper. For the last few years, however, with the greatly improved enamels now being made, up to diameters of 3 mm only enamelled magnet wire has been used.

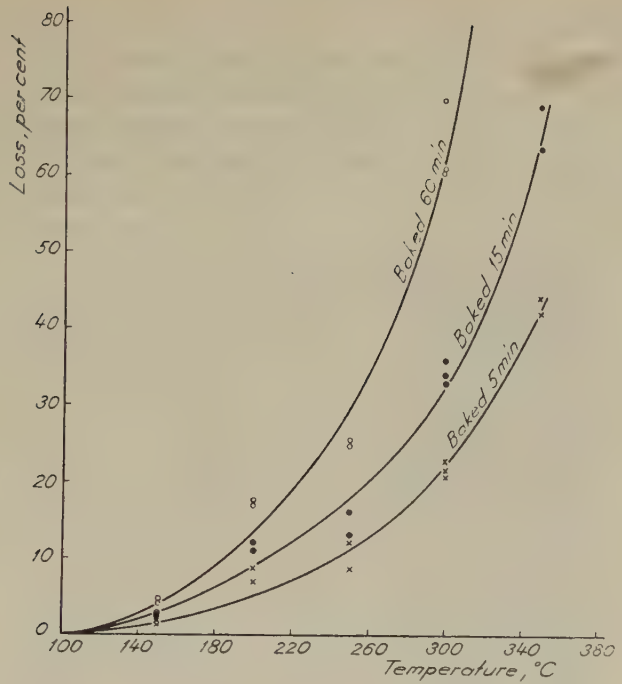

Fig. 1. Evaporation loss of oil-base enamel during baking.

The claims made on a good wire enamel are many. The enamel varnish must yield a thin, homogeneous, tough, elastic and adhesive film on the copper wire and should preferably be applicable to all kinds of wire, with diameters from 0.05 to 3 mm, or more. It should also be possible to use the varnish with different coating devices, such as rolls, wipers or dies, and in vertical as well as in horisontal baking ovens. The concentration should be high at the viscosity suitable to the enamelling equipment, thus reducing the cost of solvents and the number of coatings necessary to get the desired film thickness.

It is true that a high baking temperature eliminates the need of annealing at least the smaller wires, but on the other hand the loss of enamel due to evaporation is reduced by working at a lower temperature. This is shown by the diagram in Fig. 1, where the loss is plotted against the baking temperature according to the results of an investigation made

at the *Asea* laboratory. The temperature cannot of course be chosen too low and under service conditions the evaporation loss of an oil-base enamel has been evaluated at 35 per cent. With synthetic resin enamels the figures have been found to be even higher. Thus about 50 per cent was lost in the baking ovens in the case of a German synthetic varnish. The loss by evaporation has of course to be taken into account when calculating the enamelling costs.

As applied on the wire the enamel should be homogeneous and free from pinholes. For testing the film continuity the wire is usually passed through a mercury bath with a potential of 50—125 V between wire and mercury, the number of punctures per unit of length being registered (5, 6). There is also an apparatus constructed with three successive mercury baths, between which the wire is treated in a way similar to the winding of a coil (7). Saltwater is sometimes preferred to mercury (8), particularly for larger diameters, on account of its better wetting properties. The number of punctures is dependent on the voltage applied and it is suggested by Hanson (9) that a series of tests should be made with increasing test voltage. By a statistical treatment according to the Weibull theory of the results thus obtained a fuller view of the quality of the enamel should be obtained.

The copper is usually considered to be the cause of the pinholes and, of course, the wire to be enamelled has to be smooth and scrupulously free from stains. But the nature of the solvents is of equal importance. The solvent mixture should have a continuous boiling curve and if it is composed of solvents of different character, the components must evaporate in the correct order so that a premature deposition of the enamel does not occur. It is often advantageous to have a temperature gradient in the baking oven.

A simple test for the adhesion of enamel to copper is to stretch the wire until it breaks, but Weh (8) suggests a better method observing, however, that there is no test so far devised that is quite satisfactory. The enamel is scraped off one side and the wire is twisted on the axis of its length until the enamel film breaks and frees itself from the wire. The num-

ber of twists is an indication of the tenacity of adhesion. There are also special apparatuses for this purpose (10, 11).

Hardness and toughness are among the most desired properties of an enamel. Magnet wire is often rather roughly treated and has to withstand knocks and abrasions during the making or mounting of coils. The hardness especially depends

Fig. 2. Testing the abraison resistance of wire enamel at the *Asea* laboratory.

more or less on the baking conditions. With increased temperature and baking time the hardness increases, but so does the brittleness, and there is therefore always a maximum limit for the curing of an enamel.

The hardness may be tested and graded by means of lead-pencils according to a method proposed by Rossmann (12), but the toughness as measured by an abrasion test is of more significance. At the *Asea* laboratory the enamelled wire is repeatedly passed to and fro over a blunt edge, the wire being pressed against the edge by a roll loaded with a weight proportional to the square root of the wire diameter (Fig. 2). The number of passes made until the enamel is scratched and

until it is worn through to the copper, is noted. Similar methods are described by Staebner (13), Weh (8, 11), and Burmeister (14), but these should be called scraping rather than abrasion tests, the edge being apparently quite sharp. Weh (8) has also used a squirrel cage rotating drum with hardened rods, over which the wire is stretched by a weight proportional to the area. Investigations with this abrasion tester have shown that the abrasion resistance, for a given enamel and wire, stands in relation to the square of the film thickness. Finally a modification of the Gardner sand abrasion test (12) may be mentioned.

The hardness of course decreases with increasing temperature, and the thermoplastic behaviour of the enamel may be studied by applying the above mentioned methods at different temperatures. It has also been suggested to cross two wires between loaded plates and observe the temperature at which a short-circuit is obtained (8, 11, 14).

The solvent resistibility of the enamel is closely related to its hardness and may be investigated by measuring the change of hardness after immersion in the solvent. Other methods are described by Niesen (10), while Greulich (15) has made a careful study of the kinetics of the swelling and dissolution of an oil base enamel in different solvents.

Just as important as hardness and abrasion strength is the elasticity or flexibility of the enamel. This quality is characterised by the smallest mandrel around which the enamelled wire can be wound without cracks appearing in the enamel. The manufacture of enamelled wire is usually controlled by means of this test, which is quite a simple procedure and only necessitates a set of mandrels — or a tapered mandrel — and careful observation.

As has been shown by Hoekstra (16), not only the elasticity but also the adhesion of the enamel to the wire will influence the result of this test. The elongation of a separate oil-base enamel film was evaluated at only 3.5—19 per cent, depending on baking conditions, while deposited on a copper wire the enamel may be stretched 50 per cent without breaking. This remarkable fact explains why an enamelled wire with a thin coating will, without the enamel cracking, withstand being

wound round a much smaller mandrel than a heavily coated wire.

Curiously enough the elasticity of the enamel is reduced when heated even for a short time, and this sensitivity to "heat shock" is measured by noting the cracking of the enamel on tapered mandrel helices of the wire after heating for say half an hour at 150° C (8, 11). On the other hand, it is not surprising that the elasticity of the enamel is more or less impaired by age. The mandrel test is thus universally used to study the tendency to age. Accelerated tests are made at elevated temperatures, 90—150° C.

The requirements of a good wire enamel are not only numerous and rigorous, but also in a way contradictory. This is particularly the case with hardness and insolubility versus elasticity. As has already been stated, a hard and insoluble enamel is likely to become too brittle and a very flexible and extensable enamel is often too soft. The task will obviously be to find an enamel which simultaneously gives the film the maximum hardness and elasticity.

According to our present knowledge the elasticity of a body is due to the molecules being large and chain-like, as is the case in high polymers or polycondensates of bivalent compounds. Such straight-chain molecules are coiled and intermingled and when stretched the molecules will first uncoil and then glide along each other. The longer the molecules, the greater is the coiling tendency and the adhesion between the molecules, and consequently the elasticity. Inter- and intramolecular forces exercised by dipoles, or mechanical hindrances from side-branches or cross-linkages will tend, however, to reduce the elastic properties.

Turning to hardness and resistance to solvents, we will find that these properties, on the other hand, are improved by increasing the number of cross-linkages and polar units. Most stable, therefore, are the three-dimensional resins formed by the condensation of polyvalent compounds, such as phenol-formaldehyde or glycerine-phthalic acid resins. But such resins are altogether too brittle to be used in enamels. They must be plasticised by the introduction of long hydrocarbon chains, such as fatty acids, in the molecules.

Summarizing, we would demand from an enamel varnish that the body should be composed of long chain-like molecules, though not larger than that they will easily dissolve in the appropriate solvent. After evaporation of the solvent and at a low baking temperature these molecules should be combined with each other by a moderate number of cross-linkages, preferably by means of polar units, to form stable molecular aggregates, rendering the enamel tough and insoluble. In addition, these aggregates should contain no weak points, such as double bonds, easily attackable by oxygen and reducing the ageing stability of the enamel.

The conventional enamel for copper wire has until the last few years been made on a drying oil-base (15, 17). The varnish is prepared by heating a mixture of linseed oil and Chinese tung oil, usually in the proportion 1 to 3 (18), with a bitumnious substance or some natural or modified resin, cooling and then cutting with a kerosene or similar solvent. An often cited formula has been given by Kienle and Adams (19).

In heating the drying oils, a polymerisation takes place. The long hydrocarbon chains from different oil molecules are tied together by oxygen bridges or ring formations at the double bonds, large three-dimensional molecule aggregates being formed (20). This structure, which is further developed during baking and ageing of the enamel, should obviously meet the above stated requirements (21). Drying oil-base varnishes have also proved to be quite satisfactory for many purposes, yet hardly for magnet wire. The coatings lack the proper toughness and are never sufficiently resistant to solvents, even if the latter property may be improved by heating the enamelled wire for some time at 120° C (15, 16).

The hardness is improved by the addition of bitumen or resins, but at the same time the resistivity to solvents is impaired. This is particularly the case with bitumen, and oil-bitumen varnishes are now rare, the enamel being attacked by e. g. insulating oils (16, 22). Both copal and rosin have been used, either alone or together, and the hardness is usually improved by esterification with glycerol and lime. Lately, modified natural resins have been introduced (23). These may be prepared either by melting partly condensed phenol resins

with colophony or by the simultaneous condensation of phenol, formaldehyde and colophony or a similar resin. It has been shown that the phenol alcohols react with the double bonds in the rosin, a so called chroman ring being formed (24). These resins also should be neutralised with glycerol or lime.

By decreasing the amount of linseed oil or omitting it altogether the resistance to solvents may be further enhanced, but such varnishes are difficult to handle and are preferably used for large diameter magnet wire.

These measures have certainly lead to great improvements as regards both toughness and resistance to solvents, but the result is still not satisfactory enough for magnet wire to be used without a fabric covering. To illustrate this statement a few results from the testing of oil-base enamelled wire at the *Asea* laboratory have been compiled in Table 1. In this table, the relation between the diameter of the smallest mandrel around which the enamelled wire may be wound without cracks appearing in the enamel, and the wire diameter is given as a measure of the elasticity of the enamel. The toughness is measured by the abrasion number as obtained with the *Asea* abration tester, the enamel being just damaged, and the resistance to solvents by the same abrasion number, but the enamel being worn through, after immersion of the enamelled wire for 6 hours at 25° C in a specified impregnation varnish with a kerosene solvent. A figure less than 2 indicates that the enamel is very easily scraped off with the finger nail, 2—10 fairly easily, 11—30 only with difficulty, and when the abrasion number is higher than 30 the enamel can hardly or not be scraped off with the nail at all.

A and B are samples of enamelled wire, representative of the pre-war manufacture in Germany and Switzerland respectively. C is a wire enamelled in a vertical machine with a varnish prepared of 15 per cent linseed stand oil, 50 per cent tung oil, and 35 per cent of a resol-colophony resin, while D is enamelled in the same way with a varnish of 60 per cent tung oil and 40 per cent of a condensation product of phenol, formaldehyde and rosin.

When comparing the figures for different wires due consideration should be taken to the thickness of the enamel

Table 1.

Properties of Oil-base Enamelled Wire.

Mark	Wire diameters mm	Overall enamel thickness 10^{-3} mm	Maximum elongation [1] per cent	Abrasion number	
				as delivered	after treatment in varnish
A	0.3 —1.0	31—64	50—53	75—175	0—1
B	0.3 —1.0	37—67	31—46	95—200	0—4
C	0.25—1.0	23—65	26—40	110—200	35—90
D	0.25—1.05	28—105	31—47	90—200	20—98

[1] Calculated from the formula $100 \cdot \frac{d}{D+d}$, where d is the diameter of the enamelled wire and D is the smallest mandrel diameter, for which no cracks appear in the enamel.

film and the baking grade, as shown by the mandrel test (maximum elongation).

Oil-base enamels have no good reputation as regards ageing properties (21). Enamelled wire may, of course, be stored for years without becoming noticeably brittle (16), but this is true only if it is kept in the dark. Exposed to light, and above all to the sun, the enamel may deteriorate badly in a few months or even weeks.

At higher temperatures, enamels react very differently and there are obviously several factors exerting a more or less detrimental influence on the stability of enamel towards oxidation. The presence of drying agents is always deleterious and if siccatives are indispensable for quick curing, one must be careful to choose the right kind and use as little thereof as possible. Another important item is the nature of the resin added to the drying oils, although unfortunately very little is known about the ageing tendency of different compositions. Last but not least, the method of preparing the varnish and of baking the enamel may entirely change its reaction.

To quote an example, a very careful study of the ageing of oil-base enamelled wire in air and transformer oil was made at the *Asea* laboratory some years ago. 0.40, 0.55 and

0.75 mm copper wire was emamelled with the same varnish as C in Table 1, and in three different ways, viz. in normal thickness with two different baking temperatures (L and N) and extra thickly (T). Samples of these wires were subjected to the influence of air and transformer oil, respectively at

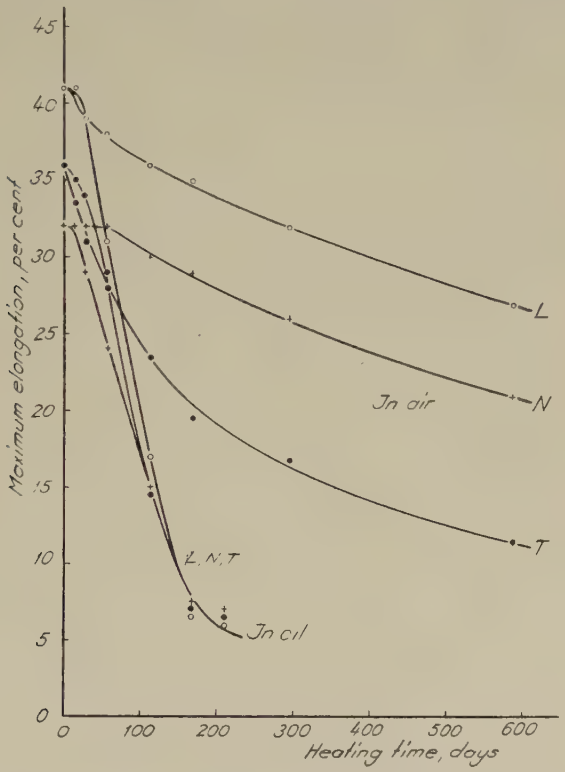

Fig. 3. Ageing curves for oil base enamels in air and transformer oil at 90° C (L = low baking temperature, N = normal baking temperature, T = thick enamel).

90° C, mandrel tests being made at suitable intervals. The results are given in the diagram in Fig. 3, where the maximum elongation of the enamel, as calculated from the mandrel test results, is plotted against time. The curves represent the average of the values obtained for the three wire diameters, these values being in close agreement with one another if the thickness of the enamel is considered.

As will be seen from Fig. 3, the enamel deteriorates much

more rapidly in oil than in air and while there is little difference between the three kinds of enamels in oil, particularly after some time, this is not so in air. There is in the beginning a sharper fall of the curve for the thick enamel but after about half-a-year all three curves run practically parallel to each other. In order to get a better idea of the influence of the enamel thickness on the deterioration due to oxidation, the maximum elongation of the enamel of all wires at the end

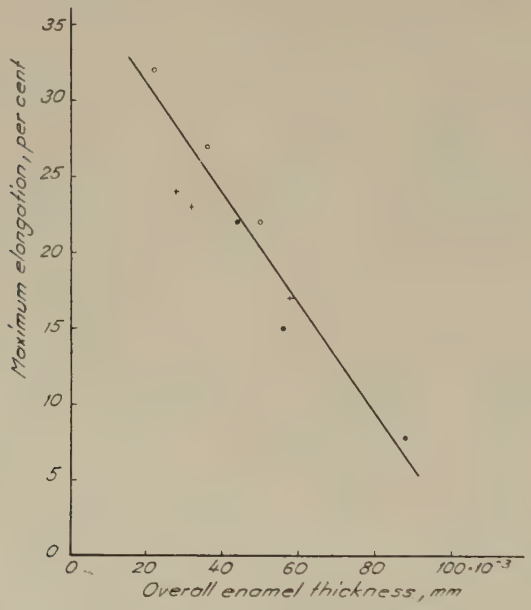

Fig. 4. Maximum elongation of enamel after 588 days at 90° C in air as a function of the enamel thickness.

of the test in air has been plotted against the enamel thickness in the diagram of Fig. 4. As is seen from this diagram the ageing of the enamel is very dependent on the enamel thickness, a thicker enamel apparently declining more markedly than a thinner. This fact, which may be due to the influence of the adhesion of enamel to copper on the mandrel test, must be born in mind when comparing the ageing properties of different kinds of enamel by means of this test.

The most striking impression of Fig. 3 is perhaps the excellent ageing properties of oil-base enamel in air. It was

shown recently, however, that the surprisingly good reaction of these samples and the close agreement between the results obtained with different wires, was more or less a chance occurrence. When a new series of ageing tests was made with other oil-base enamelled wires the results were not so good.

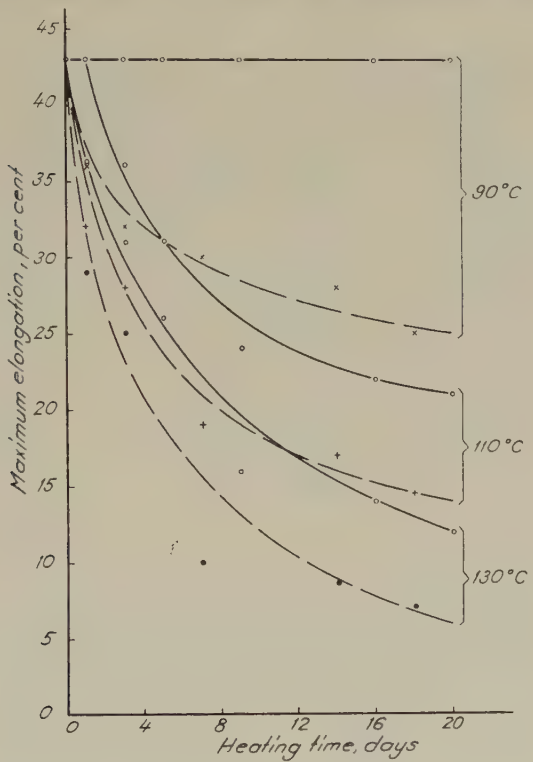

Fig. 5. Ageing curves for oil base enamels of 0.05 ± 10 % mm thickness in air at 90, 110 and 130° C, representing good and poor results.

Fortunately the old samples had been kept and the experiment could be repeated and extended to wires of other diameters. On the whole the above results could be confirmed, but other diameters of wire, enamelled at the same time, reacted quite differently even if due consideration is taken to the influence of the enamel thickness. In the diagram of Fig. 5 a few results are reported referring to an enamel thickness of 0.05 mm. Two curves are given for 90, 110 and 130° C, representing

the best and the worst results obtained with oil-base enamels of *Asea's* make.

It is obvious from Table 1 that the introduction of phenol resins has brought about a considerable improvement in oil-base enamels as regards toughness and insolubility. The tendency has consequently been to proceed in this direction. Oil-soluble phenol resins have been produced by etherification of highly reactive resols with monovalent alcohols and then reacted with, say, drying oils, yielding plasticised phenol resins with excellent film-forming properties (24). Unfortunately these products do not withstand the high temperatures used in baking wire enamels (23) and have poor resistance to ageing (25). They can therefore be used only in combination with drying oils or synthetic resins of other types, notably alkyd resin.

The phenol resins are undoubtedly particularly suited for use with Chinese tung oil but the prevailing shortage of this oil has temporarily at least checked the development on this line.

Alkyd resins include all complexes resulting from the interaction of polyhydric alcohols and polybasic acids with or without other alcohols or acids. The industrial development in USA some 30 years ago was based on the use of phthalic anhydride, which was then being produced on a large scale according to new methods, glycerol and fatty acids (26). Most alkyd resins are still made in the same way.

By a proper choice of alcohols and acids and their proportions, alkyd varnishes may be prepared yielding elastic films of outstanding heat stability (27). Alkyd resins have also been suggested for use as wire enamels (28), but apparently without success.

Experiments carried out at the *Asea* laboratory have shown that it is quite feasible to cover copper wire with alkyd enamels. Curing of alkyd resin is, however, so slow that it is out of the question to introduce this type of enamel in practice. It would of course be possible to accelerate the baking by modifying the alkyd or by the addition of drying agents,

but the ageing properties are then so impaired that the enamel cannot be accepted. Besides, the adhesion of alkyd enamels to copper seems to be rather poor.

It is an old habit of varnish makers to mix their products, and many improvements have certainly been brought about

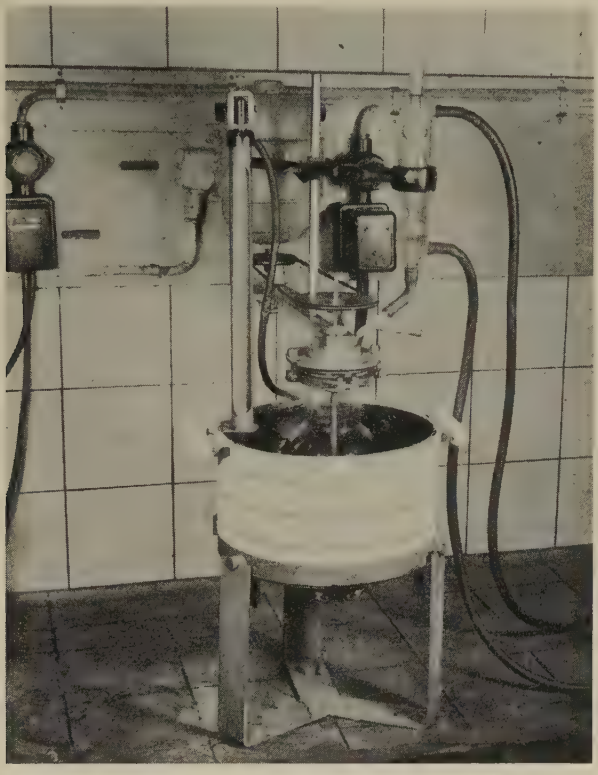

Fig. 6. Laboratory apparatus for making enamel varnishes.

in that way. According to FONROBERT this is still true of the new synthetic varnishes. The highest quality should be obtained by blending as many compatible synthetic resins as possible (23).

A well-known example is of course the combination of alkyd resins with cellulose nitrate for surface finishing. But alkyd resins have also been successfully tried with other thermosetting resins, which may help to shorten the baking time.

This has been the trend of development as regards wire enamels in Germany (25, 29).

A series of experiments on the same line have also been made at the *Asea* laboratory. The leading principle has been to get two soluble resins which react quickly at the baking temperature to yield an enamel film of the desired properties.

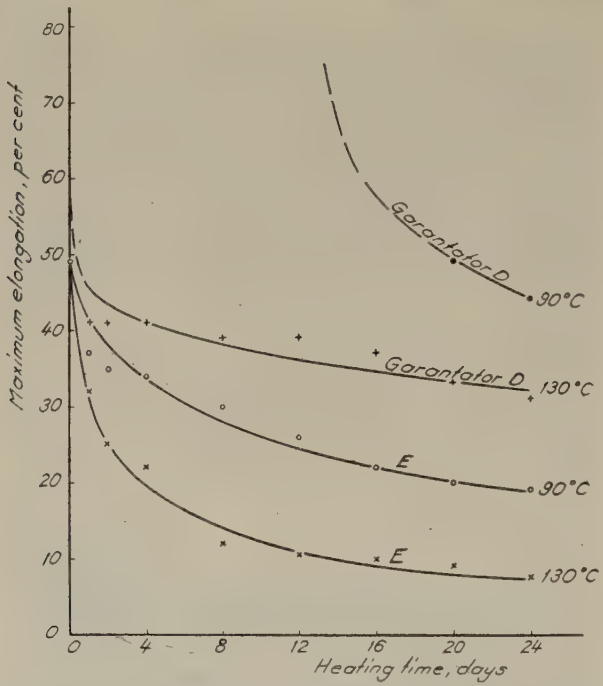

Fig. 7. Ageing curves for synthetic resin enamels in air at 90 and 130° C (E own make).

Such a reaction is the etherification between methylol and alcohol radicals. The varnishes have therefore been prepared of a primary condensation product of phenol, melamine, or urea with formaldehyde and an alkyd, the composition of which has been varied within wide limits. The best results so far have been obtained with a mixed condensate of phenol and melamine with formaldehyde and an incompletely esterified alkyd (E in Table 2).

As has been pointed out by Schäfer (21, 30), alkyd resins with adipic acid instead of phtalic anhydride yield tougher

and more elastic films, probably because of the substitution of the rigid benzene ring by a hydrocarbon chain. A German wire enamel, composed of an alkyd of this type and an alcohol substituted urea-formaldehyde resin, has been used by *Asea*. The reaction in the baking oven should be the same as above, viz. an etherification between methylol groups and alcohol radicals. As is shown by Table 2 this enamel (*Garantator D*) has far better toughness and resistance to kerosene (but not to other solvents) than has the conventional oil-base enamel.

The German enamel is superior to the oil base enamel also as regards ageing (Fig. 7) whereas this can hardly be said of type E.

Table 2.

Properties of Synthetic Resin Enamelled Wires.

Mark	Wire diameters mm	Overall enamel thickness 10^{-3} mm	Maximum elongation	Abrasion number	
				as delivered	after treatment in varnish
E	0.28—0.55	44—60	55	>200	100—200
Garantator D	0.25—1.0	40—90	>75	>200	>200
Formex	0.29—0.51	53—56	>75	>200	>200
Formal enamelled wire	0.28—0.4	18—53	>75	>200	>200
Nylon	0.35—0.9	30—59	>75	>200	>200

The appearance of quite a new type of wire enamel, based on a polyvinyl acetal, was announced in 1939 by Flynn (31) and a little later a fuller description of the characteristics of this new product was given (32).

Polyvinyl acetals are obtained from polyvinyl acetate, which is produced by the polymerisation of vinyl acetate. There is no need to isolate the polyvinyl alcohol unless an especially pure product is desired, and technically the saponification of the acetate and the subsequent acetalisation are carried out in one operation, either in an organic solvent or in dilute mineral acids. The nature of the solvent has a noticeable effect on the quality of the polyvinyl acetal (33).

Various aldehydes may be used for the acetalisation, and

the properties of the acetal are largely dependant on the nature of the aldehyde (34). The formal, i. e. the formaldehyde acetal, has the highest softening point and is most resistant to solvents. Only formaldehyde, alone or in combination with furfural, is therefore used for acetals for wire enamels. The polyvinyl formal, however, is slightly less resistant to water than the other acetals.

Among the factors affecting the properties of the polyvinyl formal are also the size and the shape of the molecules. These are primarily dependent on the corresponding properties of the polyvinyl acetate. According to Weihe (34), no change of the chain length takes place even if the reactions are carried out energetically, but McDowell and Kenyon (35) found, by a series of repeated saponifications of polyvinyl acetate to alcohol and reacetylations, a decrease of the polymerisation degree during the first cycle, presumably due to the rupture of unstable linkages in the linear molecule.

A number of experiments have been made verifying the results of McDowell and Kenyon. Polyvinyl acetates of American and German produce, (*Vinylite Ayaa* and *Ayat*, and *Mowicoll* II and *Mowilith 20*, respectively) as well as various acetates made by the *Mo och Domsjö AB*, were investigated as to molecular weights at the Institute of Physical Chemistry, University of Uppsala, the ultracentrifuge method being employed. The results are given in the diagram of Fig. 8 with the molecular weight as abscissa, and as ordinate the value of the ratio of the specific viscosity, η_{sp}, to the concentration, c, at infinite dilution in solutions of the acetates in acetone. If the molecules, as would be expected, are linear, this latter value should be proportional to the molecular weight according to the law of Staudinger (36). As is seen this is only approximately true, the deviations probably being caused by irregularities in the structure of the molecules. As a matter of fact comparative studies of the sedimentation and diffusion constants suggest that the polyvinyl acetates are in all probability more or less rolled up in balls. This fact would incidentally explain the experience that saponification and acetalisation proceed much slower when the polymerisation degree is higher.

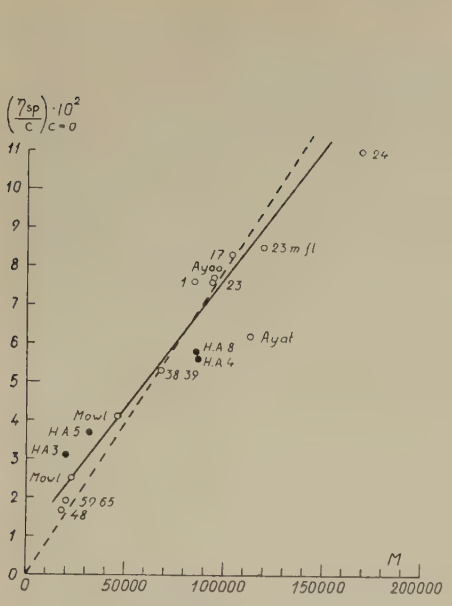

Fig. 8.

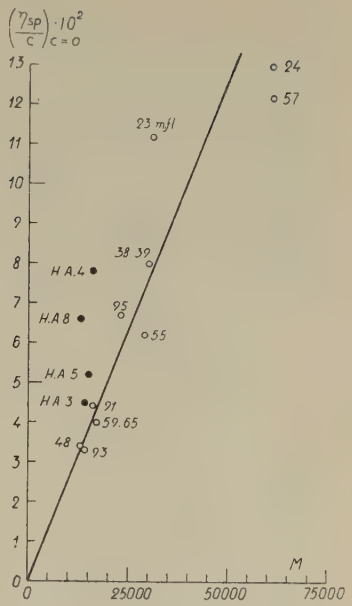

Fig. 9.

Fig. 8. Relation between viscosity and molecular weight for polyvinyl acetates according to measurements at the Institute of Physical Chemistry at Uppsala.

Fig. 9. Relation between viscosity and molecular weight for polyvinyl formals according to measurements at the Institute of Physical Chemistry at Uppsala.

The above-mentioned polyvinyl acetates have been transferred to formals and the molecular weight of these products determined in the same way. The results are plotted in the diagram of Fig. 9. They agree fairly well with the Staudinger law with one notable exception. A series of formals, HA 3, HA 4, HA 5 and HA 8, (marked with filled rings in the diagram), all four having about the same molecular weight, differ considerably as regards the value $\left(\frac{\eta_{sp}}{c}\right)_{c=0}$. The corresponding acetates, on the other hand, deviate from the Staudinger line in the opposite direction (Fig. 8).

In the diagram of Fig. 10 the polymerisation degree of the polyvinylformals is compared with the polymerisation degree of the corresponding acetates. Large molecules are obviously broken down when saponified and acetalised, in conformance

with the observation of McDowell and Kenyon. But at lower polymerisation degrees the molecules are on the contrary built up to larger aggregates, obviously due to side-branching and cross-linking between different molecules.

Another factor of importance is the polydispersity of the acetates, which has also been studied by the Institute of Physical Chemistry at Uppsala. It has been shown from variations in the diffusion constant, fractional separation and

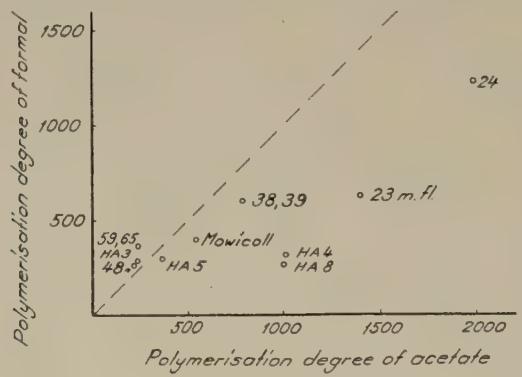

Fig. 10. Polymerisation degree of polyvinyl formals as compared with the polymerisation degree of the corresponding acetates.

adsorption analyses, that most polyvinyl acetates are rather polydispers. They are often composed of two main fractions with quite a different degree of polymerisation, and usually contain a little exceptionally low- or high-polymerised acetate.

All these factors certainly affect the properties of a wire enamel on a polyvinyl formal base, although it is not always clear how and to what degree. Long chain molecules should favour the elasticity and ductility of the enamel, but these properties seem to be good enough already at quite a low degree of polymerisation, or maybe the adhesion of the polyvinyl formal to metal, which appears to be exceptionally strong, is the dominating factor in the mandrel test. Anyhow, a great number of enamelling tests with polyvinyl formals ranging in molecular weight from 6 500 to 61 000, have shown no marked difference between the various products. There must of course exist a minimum limit as regards molecular

size, as monovinyl acetate does not yield an enamel at all, but this limit must be lower than 6 500.

A high molecular weight has the disadvantage of poor solubility. Suitable solvents for polyvinyl formals are on the whole scarce (33, 34), and for wire enamels only furfural or mixtures of furfural, alcohol, and solvent naphta have found use. In order to reduce the number of enamelling operations and the cost of solvents the varnish must have a high content of body. This condition is very difficult to fulfil with polyvinyl formals and the molecular weight should, therefore, not be higher than about 15 000. Even then it is necessary to use special devices for the application of the varnish to larger wires (32).

The influence of the structure of the molecules on the properties of the enamel is not known in detail. It appears, however, to be of no consequence if the polymerisation is effected with the acetate dissolved in an organic solvent or dispersed in water, if only the degree of polymerisation is the same. The baking of the enamel obviously results in a number of cross-linkages being established between the molecules, either over the aldehyde and alcohol remains or directly after splitting off formaldehyde. The latter reaction is supported by the observation by Weihe of the escape of formaldehyde by heating polyvinyl formal (34). A premature cross-linking between the molecules, as may take place by careless drying of the formal, should be avoided because it is accompanied by a decrease in solubility.

It has been suggested that furfural would be particularly suitable as a solvent on account of its ability to form cross-linkages between the formal molecules (37). Comparative experiments with and without furfural have, however, failed to establish a noticeable difference in the quality of the enamels obtained.

Further it has not been conclusively shown that a polydisperse product is unsuitable in other respects than that the presence of a high-molecular fraction decreases the solubility. But the best enamelling results have been obtained with formals of low polydispersity.

A partial or complete substitution of the formaldehyde to

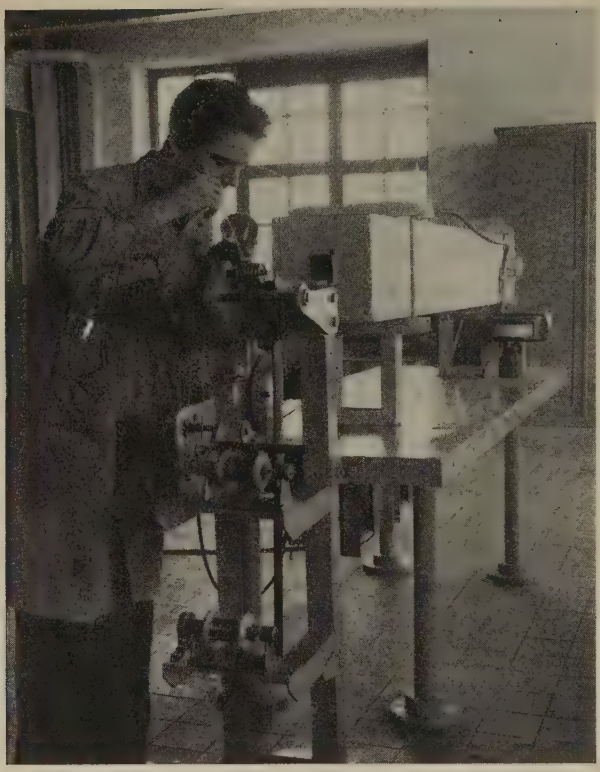

Fig. 11. Enamelling wire at the *Asea* laboratory.

acetaldehyde in the acetal base leads to a softer and more soluble enamel. The resistance to solvents is also impaired by decreasing the degree of acetalisation, and a high content of acetate groups, which according to WEIHE should have the same effect as the introduction of acetaldehyde, on the contrary makes the enamel more brittle. According to the experience gained in the experimental work at the *Asea* laboratory, the acetate content should be 10—20 per cent. With the acetalisation method adopted, the alcohol content is then about 5 per cent. The significance of the alcohol group for the establishment of cross-linkages has already been mentioned. It is possible that the alcohol content may also influence the resistance to water, which however is apparently more influenced by the method of acetalisation (33).

The properties of magnet wire enamelled with polyvinyl formal resin have been comprehensively studied by Patnode, Flynn and Weh (32), but in order to get a comparison with other enamels quoted in this survey a few data obtained at the *Asea* laboratory with *Formex* wire from the *General Electric Co.* and other formal base enamelled wire are compiled

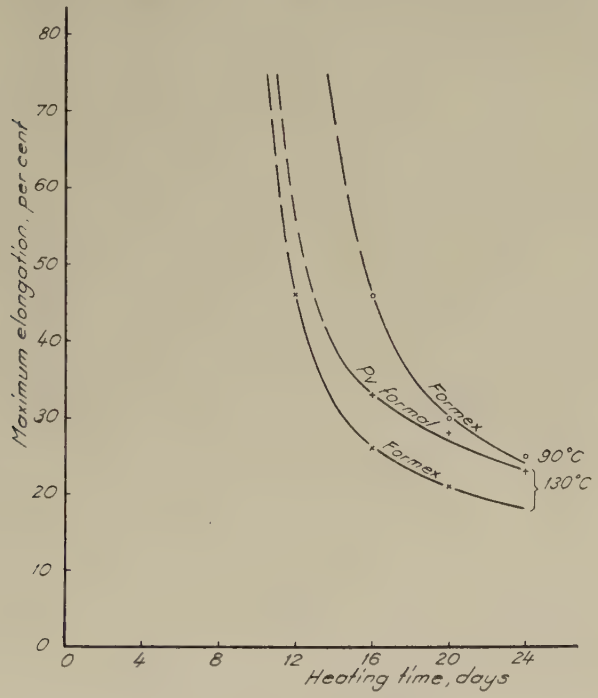

Fig. 12. Ageing curves of polyvinyl formal enamels in air at 90 and 130° C.

in Table 2. As regards toughness and resistance to solvents the polyvinyl formal resin is apparently unparallelled, although the present testing methods do not allow a discrimination between the best enamels.

As might be expected, the polyvinyl formal enamel has excellent ageing properties (Fig. 12) if properly made and baked.

The only objections to the polyvinyl formal resins are their high price and poor solubility, and in order to reduce these drawbacks experiments are being made to admix them with

other synthetic resins, following the line laid down by Fonrobert. It seems to be possible to add considerable amounts of hard alkyds, modified phenol resins or similar products without appreciably impairing the high quality of the polyvinyl formal. It is interesting to note the same trend of development abroad (38).

The polyvinyl formal belongs to the thermoplastic resins, although the high softening point and the formation of cross-linkages between the molecules in the baking process reduce the disadvantages usually connected with this type of resin.

Another example of thermoplastic resins used for enamelling wire, viz. cellulose acetate, has already been mentioned. Quite lately nylon has been tried for the same purpose (39), as is shown by Table 2, with apparent success. The trouble with the thermoplastic resins is to find a solvent for a body that has to withstand the action of the solvents used in impregnation varnishes. It is difficult to see how this task should be solved and the only practical way seems to be to cover the wire by an extrusion process. But that, to quote Kipling, is another story.

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Melamine and Melamine Resins.

By John Olsson.

Stockholms Superfosfat Fabriks A. B.

As early as the year 1834 Liebig (1) discovered, among the disintegration products from the dry distillation of ammoniumthiocyanate, a well defined substance which he called melamine and for which he gave a correct empirical formula. Later melamine has been obtained by several other methods, including the heating of cyanamide, which reaction Cloëz and Cannizzaro (2) considered to be a polymerisation of three molecules of cyanamide. Davis (3) started with dicyandiamide, which, when dissolved in aqueous ammonia and heated in a closed metal tube, is transformed by way of guanidine carbonate, ammelide and ammeline to melamine. From cyanuric chloride and ammonia Hofmann (4) prepared melamine, which he considered to be an amide of cyanuric acid. An original method has been given by Rathsburg (5), who reduced the nitration products of hexamethylenetetramine (trimethylenetrinitramine) with titanous chloride.

The technical method for the preparation of melamine takes advantage of the polymerisation of cyanamide or, better, dicyandiamide, observed by Cloëz and Cannizzaro (2), which was found by Drechsel (6) to give melamine on fusion. If this reaction proceeds at atmospheric pressure, however, the yield is very low, the greater part of the dicyandiamide decomposing with strong evolution of ammonia to give insoluble deamination products. Even if the polymerisation is carried out in a solution of dicyandiamide in aqueous ammonia under pressure, as was attempted by Stollé and Krauch (7), the yield is only 35 per cent of the theoretical. A considerable advance was made by Franklin (8), in whose experiments dicyandiamide

was dissolved in anhydrous liquid ammonia and heated for several hours under pressure about 100° C. Under these conditions the polymerisation gives a good yield of melamine without large quantities of by-products. Two circumstances are of importance here, namely that the reaction occurs in the absence of water, which otherwise gives rise to hydroxylderivates, such as ammeline and ammelide, and that it occurs under an over-pressure of an inert gas or ammonia gas of such magnitude that the splitting off of ammonia is suppressed and thus the appearance of deamination products prevented.

The development of the process into a technically practicable procedure was carried out by the *Gesellschaft für Chemische Industrie in Basel* (9). The method here applied may be described as a polymerisation of dicyandiamide, perhaps over cyanamide, to melamine. Carefully dried dicyandiamide is employed, partially dissolved in anhydrous liquid ammonia, in an autoclave with a stirring mechanism. By careful heating of the autoclave to the reaction temperature, about 130°, the exothermic polymerisation process is started, taking place under a high ammonia gas pressure of the order of 100 atmospheres. The great evolution of heat, about 25 Cal. per kg melamine, which accompanies the polymerisation, gives rise to considerable difficulties in the control of the process. An internal heat buffer, e. g. methanol, has therefore been used, giving a somewhat steadier course to the reaction. After the polymerisation is complete, the ammonia and the substance employed as heat buffer are distilled off and the melamine is obtained as a dry powdery reaction product of considerable purity. A charge of 200—300 kg melamine, prepared in an autoclave, requires about 24 hours in its production.

Since 1942 melamine has been produced in this country on the industrial scale from dicyandiamide in a manner which resembles in principle the above, but differs from it in a few important respects. It has proved more advantageous to carry out the polymerisation in a protective atmosphere of gaseous ammonia and under all circumstances to avoid a condensation of the ammonia to the liquid state. Moreover it has been possible to polymerise an autoclave charge of over 100 kg without difficulty in a few hours if it is divided among a

number of smaller vessels within the autoclave, in which, by suitably arranged heating, the reactions can be started successively. Thus the unpredictable sudden rises in temperature which otherwise occur, may be completely avoided, since a charge of corresponding size immediately enters into reaction if there is a tendency for such a rise. The pressure conditions, which are dependent upon the temperature, can therefore be governed without difficulty. It has also been found that a gaseous pressure of 45—50 atm is quite sufficient to suppress the appearance of decomposition products poor in nitrogen. The melamine yield in this technical production can be maintained at over 97 per cent, calculated on the raw material dicyandiamide.

Melamine is generally considered to be 2, 4, 6-triamino-1, 3, 5-triazine with three amino groups bound to one triazine ring, or the desmotropic form isomelamine, 2, 4, 6-triiminohexahydro-1, 3, 5-triazine. Structural formulae with mixed amino- and imino configuration have also been proposed. A characteristic feature is, however, the closed ring triazine nucleus, to which may be attributed the remarkable stability which distinguishes the melamine molecule from those of cyanamide and dicyandiamide. Melamine has a melting point of 354° and the property, very unusual in an organic substance, of being very resistant to oxidation and difficultly combustible. On careful heating to a temperature just below the melting point melamine sublimes without decomposition, while heating to higher temperatures (about 400°) causes the evolution of ammonia and the production of nitrogen-containing residues, such as melam, melem and mellon. These materials, which are very resistant towards heat, have been detected by Liebig in the decomposition products of potassium thiocyanate.

The amino groups of melamine make this compound very reactive. A brief review will now be given of the condensation products obtained when melamine reacts with formaldehyde. These are the basis of the polycondensates which constitute the melamine resins.

Even at low temperatures melamine reacts with aqueous formaldehyde to give methylolmelamines; of the six possibilities two have especially attracted interest. These are hexamethylol-

melamine and trimethylolmelamine, of which the latter is especially characterised by its great reactivity.

Hexamethylolmelamine is obtained from 1 mol. melamine and six mol. formaldehyde (or some excess), if the components are allowed to react for some minutes at 70—80° in weakly alkaline aqueous solution. It crystallises in needles with one molecule of water. Hexamethylolmelamine is quite stable when kept in the dry form.

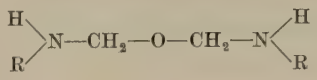
Trimethylolmelamine is obtained under similar conditions from 1 mol. melamine and 3 mol. formaldehyde, but is difficult to isolate on account of its instability. It has a marked tendency to undergo further condensation. On continued warming of an aqueous solution containing trimethylolmelamine, this condensation proceeds rapidly, which is manifested in the increase in the viscosity of the solution, the disappearance of the crystallising power, the reduction of the water solubility and the assumption of a resinous character by the reaction product. When the condensation is carried far enough, a melamine resin, amorphous, difficultly soluble in water but still fusible, is finally obtained. The resin separated from the water may finally, on thermal treatment, be converted into a completely insoluble and no longer fusible product. This final stage of the polycondensation is called "hardening" or thermosetting.

The mechanism of this polycondensation has still not been completely clarified. Köhler (10) maintains that between the crystallisable trimethylolmelamine and its amorphous polycondensate there are all possible intermediate forms. It is probable that no regular chains of rings are formed in the condensation, but primarily branched complexes, which explains the rapid disappearance of the crystallising power.

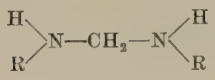
In the final stage of the polycondensation, the hardening, Köhler has shown that for each molecule of trimethylolmelamine 1.1 molecules of water and 0.4 molecules of formaldehyde are split off. This indicates that all methylol groups have reacted in a chain formation which principally occurs with the aid of ether bridges, although methylene bridges also have been formed to some extent.

Gams *et al.* (11) have also found that the ether bridges are

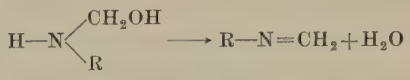
the dominating links of the longer chains in the final stage of condensation. They maintain, however, that the water, which is split off, can also indicate the forming of azomethin groups, which may work as polymerising agents.



ether bridge



methylene bridge



azomethine group

(R = diaminotriazine residue)

The hardening of the melamine resin is probably a process involving the cooperation of all these reactions in the formation of macromolecules.

The hardened final product may, if the initial material is pure, be obtained in a completely colourless, under certain conditions transparent form. Hardened melamine resin is odourless, is unaffected by water even on boiling, and is quite resistant towards organic solvents, organic acids and especially alkaline liquids. Strong mineral acids, on the other hand, have a destructive action.

In consequence of its resistance to water, melamine resin is an excellent material for electrical insulators. The surface resistance is very high, just as is the resistance to creeping currents, which is associated with the resins' high stability towards heat. It undergoes hardly any change of shape until above 150° and can be heated considerably more violently than phenol resins without any decomposition occurring. This naturally depends upon the marked stability towards heat which has already been observed in the case of melamine. Hardened condensation products of dicyandiamide and formaldehyde have considerably smaller heat resistance.

The valuable properties of the melamine resins mentioned above form the basis of their technical application for various purposes, of which only a few can be dealt with in brief.

One of these modes of employment is the use of the resin as thermosetting plastics or mouldings, which, by pressing with warm tools, can be worked into objects of the most diverse varieties. In the preparation of plastics, advantage is taken of the property of melamine resin in a water-soluble or hydrophilic phase of being intimately miscible with fillers such as wood-flour, cellulose, textile fibres etc. which can thus be completely permeated by the resin. After the drying and grinding of such a mixture, a powdered product is obtained which can be treated in a press warmed to 130—160°, when the resin undergoes its final condensation and is hardened to a compact product of permanent shape. The fillers serve to reduce the cost of the plastic; their main purpose, however, is to act as a reinforcement in the hardened material and improve its mechanical properties. From this point of view the choice of the filler is important and may greatly affect the nature of the product. The resistance to heat and water is somewhat decreased by the organic fillers. This may be avoided by the use of mineral materials such as mica powder, asbestos fibre etc. Melamine plastics may be made in any desired colours by the addition of soluble dyes or pigments. If colourless fillers such as cellulose are employed, pure white shades may be obtained, which is impossible with the phenol resins.

The manufacture of mouldings usually requires very expensive tools and thus presupposes production on a large scale if it is to be economically practicable. On the other hand the plastics are obtained in the form of objects with exact dimensions and perfect surfaces which require little or no finishing. Melamine plastics may be hardened with great rapidity, thus being superior to the phenol resins; they also harden at considerably lower temperature than do the latter.

Another form of plastic in which melamine has found application is the so-called laminated material, which is usually prepared in the form of flat plates but may also be made as tubes, cylinders or hollow bodies. For this purpose paper, wooden veneer, textile material etc. is impregnated with an aqueous solution of melamine resin. After drying, a number of such layers are pressed together between warm surfaces until the resin is completely hardened through. Such laminated

plastics are remarkable for their great resistance to water and permanence of form. They are construction materials which combine low weight with good resistant properties.

Melamine resin may be employed as a hardenable adhesive which is completely waterproof in its poly-condensed form. Here the starting material is a melamine resin in a state of condensation where it is still watersoluble. By a rapid evaporation of the solution, performed with certain precautions, the resin can be obtained in a dry and durable form, without the loss of its solubility in water. When it is used, an aqueous solution of suitable concentration and consistency is prepared. A hardening-accelerator such as potassium persulphate is often added, so that the final condensation may be carried out at low temperature in conjunction with the drying of the adhesive solution. Such a melamine resin glue may be used, for example, in the preparation of plywood, and for the attainment of a joint which is quite stable even towards boiling water.

Melamine resins of this type have also found application in the textile industry in a certain treatment of fabrics, and in the paper industry, to increase the moisture-resistance of paper.

The condensation products mentioned above might be called "pure" melamine resins. It is possible, however, to introduce other compounds or resin-forming substances during the condensation and thus to alter essentially the properties of the polycondensates.

The methylolmelamines may be etherified with alcohols, suitable agents being polyhydric alcohols which are first partially esterified with carboxylic acids (12). Such a joint condensation, often proceeding from hexamethylolmelamine, may give derivates which, in contrast to the pure melamine resins, are soluble in organic solvents such as hydrocarbons, esters, higher alcohols etc. Such ester-ether resins are valuable constituents for lacquers, which can thus be rendered heat-setting. Lacquers manufactured on a basis of melamine resin are remarkable for their high resistance to heat and oxidation, despite the fact that the hardening can be carried out at temperatures considerably lower than obtain in the case of the formerly employed "oven laquers" (13).

The condensation products of melamine and aldehydes have

been developed especially by the work of the *Gesellschaft für Chemische Industrie in Basel* (14) and of *Henkel et Cie* (15) and now constitute an important product of the modern industry of the synthetic resins, even in those countries which have good and inexpensive access to phenol resins.

The manufacture of melamine resins for different purposes has also been taken up in this country. Since our position with regard to raw materials and other factors is favourable, this should develope into a valuable branch of the young industry of synthetic resins in this country.

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Verbrennungen von chlor- und bromhaltigen Substanzen in beweglicher Bombe.

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Halogenhaltige organische Substanzen verhalten sich bei Verbrennung mit Sauerstoff ganz verschiedenartig, je nach der Art des Halogens, in der Weise nämlich, dass die Halogene in den Verbrennungsprodukten in verschiedener Form auftreten: Fluor ausschliesslich als Fluorwasserstoff, Jod ausschliesslich als freies Element, Chlor und Brom wiederum als Gemische von freiem Halogen und Halogenwasserstoff. Nur in den erstgenannten Fällen sind die Endzustände eindeutig definiert und eine Berechnung der Verbrennungswärmen der Verbindungen ohne weiteres möglich.

Bei Verbrennung der *Chlorverbindungen* führte Berthelot schon längst eine Lösung von arseniger Säure in die Bombe ein, um gebildetes Chlor zu reduzieren. Der eine von uns (Smith) konnte indessen zeigen, dass die Reduktion des Chlors jedoch unvollständig war. Die Verbrennungswärmen nach Berthelot für Chlorverbindungen sind somit zu niedrig. Zur Verbesserung der Methode wurde dann (1) vorgeschlagen, die Innenseite der Bombe mit Schlingen von mit arseniger Säure befeuchteter Quarzwolle auszukleiden. Hierdurch wurde die Oberfläche der Lösung teils sehr vergrössert teils dem Verbrennungszentrum näher gebracht. Nach Beendigung der Hauptperiode konnte auch kein Chlor mehr nachgewiesen werden. Diese Methode hat sich gut bewährt. Nach derselben sind im Lunder Institute die Verbrennungswärmen für beinahe 150 Chlorverbindungen ermittelt worden,[1] wodurch eine Reihe von wichtigen

[1] Siehe besonders die Dissertationen von Schjånberg (2), Eftring (3) und Karlsson (Karrman) (4).

Energiegrössen für solche Substanzen berechnet werden konnten, zumal für vollständig chlorierte Körper wie z. B. Tetrachlorkohlenstoff, Hexachloräthan u. s. w.

Die Quarzwollemethode (im folgenden „Qw-methode" genannt) kann als eine *statische* bezeichnet werden im Gegensatz zu der einige Jahre später von Popoff und Schirokisch (5) vorgeschlagenen *dynamischen* mit einer schaukelnden Bombe (im folgenden „Sch.-methode" genannt).[1] Die genannten Verfasser benutzen zur Reduktion auch arsenige Säure und geben an, dass die Reduktion für sowohl Chlor- wie Bromverbindungen vollständig ist. Insgesamt sind Verbrennungswärmen für 6 Verbindungen bestimmt worden, von welchen nur eine Chlor enthält, die übrigen sind Bromverbindungen. Von den Einzelheiten der Methode wird weiter unten die Rede sein.

Da es immerhin möglich war, dass in der Qw-methode trotz der erzielten Genauigkeit der Verbrennungswärmen ein *systematischer* Fehler sich verstecken konnte, schien es wünschenswert, vergleichende Bestimmungen zwischen den beiden Methoden vorzunehmen. Einen solchen Wunsch hat das »Comité permanent de thermochimie» der internationalen Union für Chemie im Anhang ihres ersten Berichtes 1936 auch ausgesprochen. Da die Qw-methode bisher nur in Lund zur Verwendung kam, schien ein derartiger Vergleich nur in Lund ausgeführt werden zu können.

Es wäre ja am einfachsten gewesen, wenn dieser Vergleich ganz einfach in der Weise vorgenommen werden könnte, dass wir dieselben Substanzen in Gegenwart von Quarzwolle verbrannten, deren Verbrennungswärme Popoff und Mitarbeiter in der Schaukelbombe bestimmt haben. Wie bereits erwähnt, haben indessen diese Autoren leider nur *eine* Chlorverbindung verbrannt! Daneben zwar 5 bromhaltige, welche aber für die Qw-methode nicht geeignet sind. Dazu kommt auch, dass die Bestimmungen von Popoff und Schirokisch nicht sehr genau sind. Sie sagen davon: „die angeführten Zahlen wollen wir ihrer absoluten Grösse nach nicht als endgültig betrachten; bei der Arbeit wurde die Hauptaufmerksamkeit auf die Ausarbeitung der Methode und weniger auf den benutzten Etalon der Ver-

[1] Die Bombe ist nach den Angaben der Autoren im Jahre 1929 konstruiert worden.

brennungswärme, sowie auf die benutzten Präparate gerichtet". Über die Genauigkeit dieser Verbrennungen siehe unten.

Unser einziger Ausweg war daher, eine Schaukelbombe in ungefährer Übereinstimmung mit der von Popoff und Schirokisch zu bauen. Hier beschreiben wir Versuche, teils mit einer solchen, teils mit einer Bombe, bei welcher die schaukelnde Bewegung durch eine rollende ersetzt worden war.

I. Versuche mit schaukelnder Bombe.

Die Konstruktion der Bombe.

Die Schaukelbombe ist an der zitierten Stelle ziemlich eingehend beschrieben. Die Bombe ruht in einem Ringe, der in einer an der Bombenwand befestigten Achse aufgehängt ist. Auf der Achse befindet sich neben der Bombe ein Rad, welches mit Hilfe von zwei Schnüren bewegt werden kann. Hierdurch wird die Bombe geschaukelt, welches nach beiden Seiten von der horizontalen Lage aus mit einer Frequenz von etwa 11 halben Schwingungen in der Minute geschieht. Die Autoren geben leider nicht an, in welcher Weise diese diskontinuierliche Bewegung rein mechanisch bewirkt wird. Die Lösung dieses Problems scheint bei einem adiabatischen Kalorimeter nicht ganz einfach zu sein. Es ist nicht vollkommen unwahrscheinlich, dass die genannten Schnüre ganz einfach mit der Hand gehoben worden sind, ein Vorgehen, das wohl bei qualitativen Versuchen genügen kann, nicht aber bei quantitativen, wo eine genaue Reproduktion der Bewegung unerlässlich ist.

Die von uns für diesen Zweck benutzte Vorrichtung ist in den Figuren 1—3 abgebildet, und geht am deutlichsten aus Fig. 3. hervor. Die Vorrichtung gestattet zwar nicht eine Hebung der Bombe bis zur horizontalen Lage, sondern nur zu einem Winkel von 50° von der vertikalen Stellung. Durch eine Vermehrung der Schwingungsfrequenz von 5,5 (nach Popoff—Schirokisch) zu 25 ganzen Schwingungen haben wir jedoch eine gute Reduktionswirkung bewirken können (siehe unten).

Einige Einzelkeiten in der Methodik mögen noch erwähnt werden. Das Kalorimeter arbeitet isothermisch. Es befindet sich in einem Zimmer, dessen Temperatur auf $\pm$ 0°,1 konstant ist. Das Aussengefäss ist grösser als gewöhnlich: Totalvolumen 43 Liter; Temperatur mit Kühlschlange und Heizelement nebst Kontaktthermometer auf $\pm$ 0°,01 konstant gehalten. Das Innengefäss (Fig. 2) hat eine ovale Form und ist auch grösser als gewöhnlich: Wasserwert etwa 4900 cal, sonst etwa 3100. Bombe von Julius Peters, mit Platin ausgekleidet und mit Platinschild versehen. Vor dem Anfang der Verbrennung wird die Temperatur auch im Innengefäss durch elektrische Heizung genau eingestellt.

Die Schaukelbewegung wird durch die Scheibe *I* (Fig. 1) bewirkt, durch deren Umdrehung mit konstanter Geschwindigkeit der Arm *J-K-U-T* (siehe die Figuren) vertikal bewegt wird. Der Teil *U* ist aus isolierendem Material verfertigt. Die Bombe ist in einem Ringe so aufgehängt, dass der Schwerpunkt des Systems sich etwa ein Millimeter unter der Linie durch das Zentrum der Achse befindet. Die Bombe ist bis in die Nähe des Kontaktes *R-S-T* im Wasser versenkt.

Die Bestimmung der Friktionswärme.

Die ohne Zweifel grösste Fehlerquelle bei einer Apparatur wie der soeben beschriebenen ist die Friktionswärme. Popoff und Schirokisch haben keine Angaben über die Grösse dieser Wärmetönung. Um bei unserem isothermen Kalorimeter dieselbe zu bestimmen, verfuhren wir in der folgenden Weise.

30 Sekunden (ein Intervall) nach der Zündung wird die Schaukelbewegung in Gang gesetzt und dauert 3,5 Minuten fort. Nach im ganzen 4,5 Minuten beginnt die Nachperiode, die 4,5 Minuten andauert. Diese Nachperiode gibt uns die durch *Strahlungsverlust* verursachte Gangänderung (G). Dann wird das Schaukeln von neuem in Gang gesetzt während 3,5 Minuten, und eine neue Gangänderung kann errechnet werden ($G_{\text{Sch.}}$), welche grösser ist als G, weil wir so arbeiten, dass diese Grösse immer negativ ist und das Schaukeln eine Wärmezufuhr bedeutet. Das Schema für eine Verbrennung gestaltet sich somit folgendermassen:

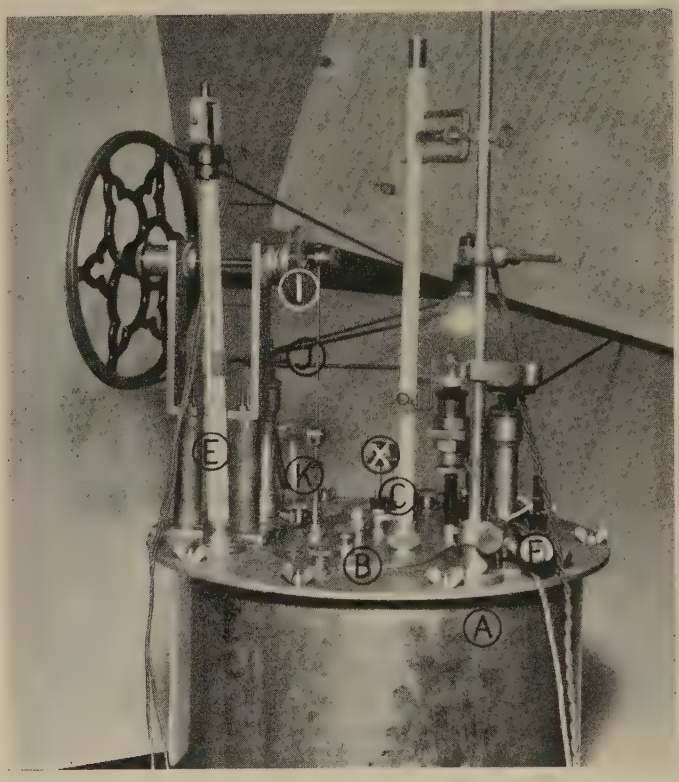

Fig. 1. Das Kalorimeter fertig für Gebrauch.

Vorperiode	0—4,5 Min.	9 Intervalle
Hauptperiode	5—9,5 »	9 »
Zündung	5 »	
Schaukeln beginnt . . .	5,5 »	
» beendigt . .	9 »	
Nachperiode	10,0—14,5 Min.	9 Intervalle
Schaukelperiode	15 —19,5 »	9 »
Schaukeln beginnt . .	15,5 »	
» beendigt . .	19 »	

Der Unterschied $(G—G_{\text{Sch.}})$ ist die pro Intervall für Friktionswärme anzubringende Korrektionsgrösse, welche, mit der Anzahl Schaukelintervalle während der Hauptperiode multipliziert, die totale Korrektion für die Friktionswärme gibt. Ein Beispiel mag angeführt werden:

Die Bezeichnungen in den Figuren 1—3 bedeuten:

A Aussengefäss,
B Aussendeckel,
C Beckmannthermometer,
E Kontaktthermometer,
F Kontrollampe für Heizelement im Aussengefäss,
I Scheibe für die Schaukelbewegung,
J und *K* Treibstangen,
O Innengefäss,
P Ring für die Aufhängung der Bombe,
R Treibstange, am Ring *P* fixiert,
S—*T* gewinkelte Treibstange,
U isolierter Teil der Treibstange,
W Schraubenmutter für das Achsenlager,
X Kontakt für die Zündung.

Fig. 2. Innengefäss nebst Bombe.

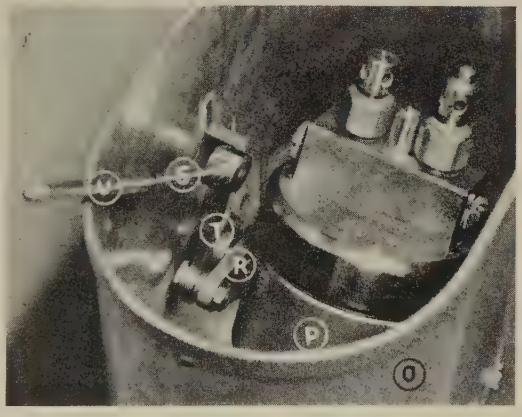

Fig. 3. Ein Detail des Treibstangensystems.

Nachperiode: . . . . 1°,6020, 20, 15, 10, 05, 05, 00, 1,5990, 90, 85°
Schaukelperiode: . . 1,5985, 80, 80, 75, 75, 75, 70, 65 60
↑ Anfang ↑ Ende

$G = -0°,00041$; $G_{Sch.} = -0°,00028$; $\Delta = -0°,00013$

Korrektion für Friktionswärme: $9 \cdot (-0,00013) = -0°,0012$.

Die Grösse der Korrektion hängt von der Schaukelamplitude und noch mehr von der Frequenz ab, und sie wächst mit beiden, wie zahlreiche Versuche ergaben. Wir haben immer mit der grössten Amplitude (50°) und der kleinsten Frequenz (25/min.) gearbeitet. Es zeigte sich jedoch, dass diese Korrektion nicht immer genau reproduzierbar war. Besonders war dies der Fall bei Trolitachsenlager (Verbrennungen von p-Dichlorbenzol und meta-Dichlorbenzoesäure unten). Viel kleiner und besser reproduzierbar wurde sie nach Einführung von konischen Stahllagern (bei den Verbrennungen von Trichlorbenzol unten). Die Friktionskorrektion ist überall in den Tabellen angegeben.

Die Vollständigkeit der Chlorreduktion.

Wir haben qualitative Versuche nach der Methode von Popoff—Schirokisch (Bewegung mit der Hand) gemacht, um die Vollständigkeit der Reduktion zu prüfen. Es stellte sich heraus, dass bei einer Amplitude von *90°* und einer Frequenz von 6 ganzen „Schwingungen" in der Minute freies Chlor nach 4 Minuten nicht mehr nachgewiesen werden konnte. Mit den von uns benutzten kleineren Amplituden und grösseren Geschwindigkeiten konnten wir indessen folgendes feststellen. (Die Chlorbestimmungen wurden durch Gasanalysen ermittelt). Bei grösster Amplitude, niedrigster Frequenz (siehe oben) und 30 Atm. Sauerstoffdruck war alles Chlor nach 4 Minuten verschwunden. Versuche mit Trichlorbenzol, das von den benutzten Substanzen den grössten Chlorgehalt hat, ergaben, dass nach 3,5 Minuten nur 3 ‰ des totalen Chlorgehalts in freiem Zustande vorhanden waren. Bei kleinerem Drucke, kleinerer Amplitude und niedriger Frequenz fanden wir 1—5 ‰ Chlor nach 4 Minuten. Da die Schaukelperiode nach 3,5 Minuten beendigt wird, ist es somit wahrscheinlich, dass zu dieser Zeit bei grossem Chlorgehalt noch so viel freies Chlor (bis zu 3 ‰) vorhanden ist, dass die gefundenen Verbrennungswärmen ein wenig zu niedrig werden: für Chlorbenzoesäure werden 0.5 cal. berechnet, für Dichlorbenzol etwa 1 cal und für Trichlorbenzol 1—1,5 cal. *Diese Fehler sind zu vernachlässigen neben anderen Versuchsfehlern.*

Die Geschwindigkeit der Verbrennung.

Die Schaukelbewegung beginnt, wie oben angegeben, 30 Sek. nach der Zündung. Es erhebt sich dann die Frage: ist die Verbrennung beendigt, wenn die Bewegung beginnt? Ist dies nicht der Fall, wird die Verbrennung durch das Schaukeln unterbrochen, da dieses ein Aufspritzen der Reduktionslösung in den Verbrennungstiegel bewirkt, der allmählich zu etwa einem Drittel gefüllt wird (entsprechend 1—2 gr Wasser). Auch wenn die Verbrennung beendigt wäre, könnte das Aufspritzen doch einen kleinen Fehler verursachen, in dem Falle nämlich, wo die im Tiegel befindliche Lösung, die ja gewissermassen thermisch isoliert ist, am Ende der Hauptperiode noch eine Temperatur hat, die höher ist als diejenige der Umgebung. Je kleiner die Verbrennungsgeschwindigkeit, um so wahrscheinlicher und grösser wäre ein solcher Fehler.

Die Möglichkeit, dass die Verbrennung nach 30 Sekunden noch nicht abgeschlossen wäre, haben wir durch Verbrennungen mit 30 Sekunden verspäteter Zündung untersucht (siehe Tab. 8). Die Verbrennungswärmen sind unverändert geblieben, eine Tatsache, die auch zeigt, dass der „Aufspritzfehler" zu vernachlässigen ist.

Die Möglichkeit, dass verschiedene Substanzen mit sehr verschiedener Geschwindigkeit verbrennen könnten, haben wir wiederum mit den hier untersuchten Substanzen durch Widerstandsmessungen in der Umgebung des Verbrennungstiegels geprüft. Wir fanden: nach 15 Sek. eine Temperatur von etwa 450°, nach 30 Sek. (Beginn des Schaukelns) etwa 120°. Thermoelektrische Messungen am Platinschilde, der oberhalb des Tiegels befestigt ist, bestätigten diese Resultate. Innerhalb der von uns erreichten Versuchsgenauigkeit hatten die untersuchten Substanzen dieselbe Verbrennungsgeschwindigkeit.

Bestimmungen von Verbrennungswärmen.

Die Methodik der Verbrennung von chlorhaltigen Substanzen ist in der Dissertation von Schjånberg beschrieben (2). Für 2 von den hier untersuchten Verbindungen hat Karlsson-Karrman früher die Verbrennungswärmen nach der Qw-me-

thode bestimmt (4). Er hat uns diese Präparate freundlichst zu Verfügung gestellt.

Die Temperaturerhöhung wurde immer zwischen 1,1°—1,2° gehalten. Bei halogenhaltigen Verbindungen muss Paraffinöl zugesetzt werden: Verbrennungswärme pro gr = 11 000 cal.

Um die Zuverlässigkeit der Sch.-methode zu kontrollieren, haben wir zuerst eine chlorfreie Substanz verbrannt und zwar Benzoesäure von KAHLBAUM, ein Präparat, das wir im übrigen zu Verbrennungszwecken nicht benutzt haben: von der Firma war die Verbrennungswärme 6322 cal/g angegeben worden.

In den Tabellen bedeuten: g Gewicht der Substanz in mg; g_1 Gewicht des Paraffinöls; $\Delta_{Korr.}$ Korrektion in Graden für die Friktionswärme; $\Sigma_{Korr.}$ = die Summe der Korrektionen (in cal) für elektr. Zündung, gebildete Salpetersäure, verbrannten Zündungsfaden (ev. Zellophan) und (bei Chlorverbindungen) gelöstes Platin und Gold; $Cl_{Korr.}$ Korrektion für reduziertes Chlor (in cal); Q Verbrennungswärme pro Gramm; Q_w Wasserwert.

Tabelle 1.

(Benzoesäure).

g	$\Delta_{Korr.}$	$\Sigma_{Korr.}$	Q
875,90	+0°,0001	−11,7	6322
875,80	−0°,0004	−11,4	6319
867,72	+0°,0003	−11,2	6322

Mittel: $Q = 6321$ cal/g; $Q_w = 4886$ (siehe unten).

m-Chlorbenzoesäure.

Verbrennungswärme nach K. J. KARLSSON (Qw-methode): 4685 ± 1 cal/g.

Bestimmung des Wasserwertes (Benzoesäure Merck: Q=6311).

Tabelle 2.

g	$\Delta_{Korr.}$	$\Sigma_{Korr.}$	Q_w
884,30	−0°,0021	−6,6	4888
886,90	−0°,0020	−6,1	4885
886,65	−0°,0026	−7,0	4888
887,67	−0°,0024	−6,6	4887
887,25	−0°,0027	−7,0	4894

Mittel: $Q_w = 4888{,}5 \pm 1{,}5$ cal/g.

Die Friktionswärme ist hier verhältnissmässig bedeutend, aber gut reproduzierbar. Vgl. Tab. 3., wo eine viel grössere Korrektion plötzlich auftritt, *ohne jedoch den entsprechenden Q-Wert merkbar zu verändern!*

Tabelle 3.

(m-Chlorbenzoesäure).

g	g_1	$\triangle_{Korr.}$	$\Sigma_{Korr.}$	$Cl_{Korr.}$	Q
777,15	180,27	−0°,0005	− 9,9	−11,9	4687
789,45	180,50	−0°,0016	−11,3	−10,9	4674
780,30	180,73	−0°,0034	− 7,8	−12,0	4674
773,79	179,37	−0°,0015	−11,7	−17,2	4673
775,90	200,80	−0°,0001	−16,7	−14,5	4683

Mittel: $Q = 4678 \pm 3{,}8$ cal/g.

p-Dichlorbenzol.

Präparat von K. J. Karlsson (Qw-methode): $Q = 4773 \pm 1$ cal/g.

Tabelle 4.

g	g_1	$\triangle_{Korr.}$	$\Sigma_{Korr.}$	$Cl_{Korr.}$	Q
513,90	294,03	−0°,0014	− 8,3	−19,1	4767
490,12	278,87	−0°,0016	−89,1	−18,7	4782
509,22	275,10	−0°,0019	−10,1	−21,7	4777
501,88	288,76	−0°,0013	−11,2	−17,0	4755

Mittel: $Q = 4770 \pm 6$ cal/g.

1,2,4-Trichlorbenzol.

Die Verbindung wurde aus chloriertem Benzol durch wiederholte Destillationen dargestellt. Analyse: Chlor ber. 58,64 %; gef. 58,76 und 58,56 %. Verbrennungen wurden sowohl nach der Qw- als auch nach der Sch.-methode ausgeführt. Wegen des hohen Chlorgehalts ist es notwendig, grössere Mengen Paraffinöl zuzusetzen als bei Chlorbenzoesäure und Dichlorbenzol, so dass von der totalen entwickelten Wärmemenge

sogar etwa 3/4 von der Verbrennung des Paraffins herrühren. Daher ist die Genauigkeit hier kleiner als bei den übrigen Substanzen. Der von der Friktion herrührende Fehler ist hier (Tab. 7) infolge verbesserter Konstruktion (siehe oben) kleiner als oben und die Korrektion besser reproduzierbar. Wir führen hier einen Auszug einer Wasserwertsbestimmung an, um dies überzeugend zu zeigen (Tab. 5).

Tabelle 5.

$\Delta_{\text{Korr.}}$	$-0°,0020$	$-0°,0007$	$-0°,0008$	$-0°,0014$	$-0°,0015$	$-0°,0018$
Q_w	4888	84	78	91	76	86

Mittel: $Q_w = 4884 \pm 2$ cal/g.

Verbrennung von Trichlorbenzol nach der Qw-methode in Tabelle 6.

Tabelle 6.

g	g_1	Korr.	$Cl_{\text{Korr.}}$	Q
354,20	392,75	−13,3	−21,3	3671
358,95	370,75	−13,7	−22,3	3691
332,60	373,80	−12,1	−20,8	3698
329,40	383,15	−11,7	−16,3	3710
331,15	345,05	−12,9	−16,8	3694

Mittel: $Q = 3693 \pm 6$ cal/g.[1]

Tabelle 7 und 8 enthalten Verbrennungen von Trichlorbenzol nach der Sch.-methode. Im letztgenannten Versuch wurde das Schaukeln 60 Sek. (statt wie sonst 30 Sek.) nach der Zündung begonnen. In der gleichen Weise wurde der Wasserwert bestimmt: gefunden (für Tab. 8) 4886 ± 1 cal/g; vgl oben 4884 ± 2.

[1] Der verhältnissmässig grosse Fehler bei dieser Substanz zeigt, dass wir die Qw-methodik nicht so gut beherrschen wie Karlsson, Schjånberg u. a., die mit derselben eine grosse Zahl von Verbrennungen gemacht haben. Der Fehler wird eben hier — wie schon erwähnt — dadurch vergrössert, dass Paraffinöl wegen des hohen Chlorgehaltes in beträchtlicher Menge zugesetzt werden muss.

Tabelle 7.

g	g_1	$\triangle_{Korr.}$	$\Sigma_{Korr.}$	$Cl_{Korr.}$	Q
333,95	369,30	−0,0005	−12,7	−16,0	3680
346,20	362,40	−0,0006	−12,5	−24,2	3690
325,35	396,20	−0,0007	−12,7	−14,7	3679
329,75	375,10	−0,0007	−13,7	−18,7	3673

Mittel: $Q = 3680 \pm 3$ cal/g.

Tabelle 8.

g	g_1	$\triangle_{Korr.}$	$\Sigma_{Korr.}$	$Cl_{Korr.}$	Q
330,45	375,85	−0,0006	−11,5	−16,7	3681
320,90	384,85	+0,0008	−15,6	−14,6	3693
312,20	364,05	−0,0006	−14,5	−18,1	3671

Mittel: $Q = 3682$ cal/g.

Die Verbrennungswärme ist wie ersichtlich bei später angefangenem Schaukeln unverändert geblieben. Als Mittel aus Tabellen 7 und 8 resultiert: $Q = 3681 \pm 3$ cal/g.

Zusammenfassung.

Wir korrigieren die Werte der Sch.-methode für die kleine Unvollständigkeit der Chlorreduktion (siehe s. 358) und stellen dann folgende Vergleichstabelle zusammen.

	m-Chlorbenzoesäure	p-Dichlorbenzol	Trichlorbenzol
Qw-methode . . .	4685	4773	3693
Sch.-methode . .	4678	4771	3682

Die Werte der Sch.-methode sind durchgehend ein wenig niedriger was besonders bei Trichlorbenzol der Fall ist. Der Unterschied liegt in der Nähe der Versuchsfehler. Die Ursache dieses Unterschiedes könnte aber ebensogut — ja vielleicht mit grösserer Wahrscheinlichkeit — in der Sch.-methode liegen als in der Qw-methode, denn diese ist ja bei so vielen Verbindungen mit sehr wechselnden Chlorgehalt geprüft

worden, und die erhaltenen Verbrennungswärmen haben bei den verschiedensten Berechnungen von Energiegrössen niemals zu widersprechenden Resultaten geführt. Durch die unten zu besprechenden Versuche mit der rotierenden Bombe haben wir die Richtigkeit eines solchen Schlusses zeigen können.

II. Versuche mit rotierender Bombe.

Der Gedanke, die Schaukelbewegung in eine rotierende zu verwandeln, um dadurch die bewegliche Bombe zu verbessern, ist nicht neu; u. a. hat Roth (6) angegeben, er habe in Zusammenarbeit mit der Firma F. Hugershoff, Leipzig, „ein neues Modell eines Calorimeters mit rotierbarer Bombe konstruiert, das sich bewährt hat; doch können noch keine definitiven Resultate angegeben werden". In einem Brief an einen von uns (Smith) hat Roth neuerdings kurz mitgeteilt, dass Versuche mit chlorhaltigen Verbindungen in einer solchen Bombe jetzt angefangen worden sind.

Die von uns benutzte rotierende Bombe wurde von dem einen von uns (Sunner) konstruiert, der die Absicht hatte, mit Hilfe derselben eine Untersuchung der Verbrennungswärmen von schwefelhaltigen Substanzen aufzunehmen. Es schien uns indessen zweckmässig, diese Bombe auch für Chlor- und besonders für Bromverbindungen zu prüfen. Die Letztgenannten können nach der Qw-methode nicht verbrannt werden, da die Reduktion des in grossen Mengen gebildeten Broms unvollständig wird. Die Verbrennungswärmen für 5 Bromverbindungen, die Popoff und Schirokisch mit ihrer Schaukelbombe bestimmt haben, sind als sehr unsicher zu betrachten.

Die ausführliche Beschreibung der Konstruktion wird an anderer Stelle folgen. Hier mag nur kurz folgendes angebeben werden. Die Bombe ist wie beim Schaukeln in einem breiten, nicht zu engen Ringe aufgehängt, welcher an der beweglichen Achse befestigt ist. Treibstangen u. dgl. sind weggelassen. Um zu verhindern, dass die Bombe beim Umkippen zur horizontalen Lage im Ringe verschoben werde, wird unter dem breiten Ringe ein anderer schmaler, *an der Bombe abnehmbar* festgeschraubt. Das Umkippen wird durch den Zug eines

dünnen Kupferdrahts bewirkt, der in Windungen um die Bombe gewickelt ist und nachher durch fortgesetzten Zug auch ein langsames Rotieren der Bombe zustande bringt: 10 Umdrehungen in 2 Min. 15 ± 1 Sek. Durch eine einfache Sperre wird die Bombe in horizontaler Lage gehalten.[1] Der Kupferdraht geht durch Löcher in den Deckeln und wird mechanisch gehoben. Die Feuchtigkeitsmengen, die der Draht aus dem Kalorimeterwasser mit sich nach oben bringt, sind unsichtbar. Der von diesem Wasserverluste herrührende, mögliche Fehler geht übrigens im Wasserwerte ein, was auch der Fall ist mit der Friktionswärme, die nicht besonders bestimmt wird und auch nicht, wegen ihrer Kleinheit, bestimmt werden kann.

Die Metallkorrektionen sind bei Verbrennung von bromhaltigen Substanzen kleiner als bei chlorhaltigen. Der Verbrennungstiegel wird bei den ersteren im allgemeinen nicht angegriffen. Bei den hier untersuchten Brombenzol und Bromnaphtalin ist die Metallkorrektion zu vernachlässigen; bei Äthylenbromid ist sie auch sehr klein, und wurde durch Bestimmung der gelösten Metalle zu etwa 0,1 cal geschätzt. Bei den chlorhaltigen Verbindungen bestimmten wir die Metallkorrektion in gewöhnlicher Weise (vgl oben).

Der bei weitem grösste Teil des in der Halogenverbindung vorhandenen Broms wird bei der Verbrennung freigemacht (siehe die Tabellen unten) und wird dann von der arsenigen Säure reduziert. Die Wärmekorrektion ($Br_{Korr.}$) für diese Reduktion ist ziemlich bedeutend. Wie bei chlorhaltigen Substanzen muss auch hier für die Wärmetönung der Oxydation von arseniger Säure zu Arsensäure korrigiert werden. Die Wärmetönung wird gewöhnlich zu 19,6 cal/Milliäquv. angegeben, ein Wert, den wir bei den Chlorverbindungen auch benutzt haben. Eine experimentelle Bestimmung der Wärmetönung für die Reaktion: $Br_2 + As_2O_3$ (beide in etwa 0,2-n Lösungen), wobei wir 13,3 cal/Milliäquv. fanden, gab uns jedoch Anleitung zu vermuten, dass der Wert 19,6 etwas zu hoch ist: 19,3 wäre vielleicht richtiger und stimmt auch besser mit aus der neueren Literatur verfügbaren Reaktionswärmetönungen.

[1] Hier mag auch erwähnt werden, dass es möglich ist, durch eine zweite Sperre die Bombe mit dem Deckel etwa 35° nach unten geneigt rotieren zu lassen, was für Verbrennungen von Schwefel-, nicht aber von Halogenverbindungen von Bedeutung ist.

Zunächst folgen die Verbrennungstabellen, zu welchen wir zuerst folgendes bemerken wollen. Der Wert von $\Sigma_{Korr.}$ ist viel grösser in den Tabellen 9—11 als in den oben angeführten und in Tabelle 12, was davon herrührt, dass die Verbrennungen in den Tabellen 9—11 wegen der Flüchtigkeit der Substanzen mit über dem Tiegel gespanntem Zellophanpapier ausgeführt worden sind. Die Korrektion für die Verbrennung des Zellophans beträgt etwa 100 cal. — Der Wasserwert des Kalorimeters betrug in allen Versuchen 4697 cal/grad.

Äthylenchlorhydrin: Substanz in Vakuum zweimal destilliert; Cl: ber. 44,04 %; gef. 1) 44,14 %, 2) 44,10 %.

Tabelle 9.

g	g_1	$\Sigma_{Korr.}$	$Cl_{Korr.}$	Q	$\frac{Cl \cdot 100}{\Sigma Cl}$ [1]
401,00	360,15	−113,6	−24,3	3604	25
393,20	352,25	−111,6	−21,4	3606	22
600,85	212,10	−113,8	−46,3	3606	32
396,85	349,95	−113,0	−24,9	3601	26

Mittel: $Q = 3604 \pm 1$.

Äthylenbromid: Substanz wie eben erwähnt destilliert; Br: ber. 85,07 %; gef. 1) 84,82 %, 2) 84,98 %.

Tabelle 10.

g	g_1	Korr.	$Br_{Korr.}$	Q	$\frac{Br \cdot 100}{\Sigma Br}$ [1]
513,00	406,85	−118,4	−102,3	1584	96 %
481,95	400,95	−104,2	− 96,5	1589	96 %
471,53	408,60	−115,7	− 94,4	1588	96 %
481,60	404,22	−117,1	− 96,8	1591	96 %

Mittel: $Q = 1588 \pm 1{,}5$ cal/g.

Brombenzol: Substanz wie oben destilliert; Br: ber. 50,90 %; gef. 50,77 %; $D_4^{20} = 1{,}4954$; $n_D^{20} = 1{,}5598$, welche Konstanten gut mit den Angaben der Literatur übereinstimmen.

[1] Diese Kolumne gibt den Prozentgehalt reduziertes Halogen an.

Tabelle 11.

g	g_1	$\Sigma_{Korr.}$	$Cl_{Korr.}$	Q	$\frac{Br \cdot 100}{\Sigma Br}$
616,25	212,42	−114,3	−74,5	4746	97
607,63	212,67	−113,0	−73,1	4742	96
615,72	206,00	−115,0	−74,1	4742	96
608,80	209,10	−111,8	−73,0	4743	—

Mittel: $Q = 4743 \pm 1$ cal/g.

α-Bromnaphtalin: Substanz wie oben destilliert; Br: ber. 38,59 %; gef. 1) 38,60 %, 2) 38,76 %; $D_4^{20} = 1{,}4826$; $n_D^{20} = 1{,}6580$; betreffs der Richtigkeit dieser Konstanten vgl oben.

Tabelle 12.

g	g_1	$\Sigma_{Korr.}$[1]	$Br_{Korr.}$	Q	$\frac{Br \cdot 100}{\Sigma Br}$
948,80	0	7,8	86,4	5802	96
913,50	0	9,7	83,6	5797	97
687,50	122,05	8,7	62,3	5803	96
697,45	110,05	8,9	63,9	5800	—

Mittel: 5800,5 ± 1,5 cal/g

Wir vergleichen zuerst die für Äthylenchlorhydrin und Äthylenbromid hier gefundenen Werte mit denjenigen von Popoff und Schirokisch (P—S)

	S—S	P—S
Äthylenchlorhydrin	3604 ± 0,03 %	3537,5 ± 0,1 %
Äthylenbromid	1588 ± 0,1 %	1546,7 ± 0,5 %

Die russischen Autoren führen keine Originalziffern an und beanspruchen auch nicht — vgl oben — dass die absolute Grösse ihrer Verbrennungswärmen endgültig sein sollen. Wir meinen auch dass die von uns gefundenen, etwa 2 % höheren Werte die richtigen sind und sie sind *überhaupt die ersten einigermassen einwandfreien Verbrennungswärmen für Bromver-*

[1] wie oben bemerkt, ohne Zellophan verbrannt.

bindungen, die bis jetzt veröffentlicht worden sind. Man kann in folgender Weise auch eine Vorstellung von der Genauigkeit derselben geben.

Die molekularen Verbrennungswärmen (Q_M) für folgende Verbindungen werden zusammengestellt und ihre Differenzen (Δ) berechnet. — Für Chlor- und Jodverbindungen sind die Werte aus Karlssons (Karrman) Dissertation entnommen.

	Q_M		Q_M
Chlorbenzol	742,95 Kal	α-Chlornaphtalin	1197,14 Kal
	$\Delta = -1{,}70$		$\Delta = -3{,}56$
Brombenzol	744,65 Kal	α-Bromnaphtalin	1200,70 Kal
	$\Delta = -18{,}11$		$\Delta = -16{,}85$
Jodbenzol	762,76 Kal	α-Jodnaphtalin	1217,55 Kal

Wie ersichtlich stimmen die Δ-Werte, die ja kleine Differenzen zwischen grossen Zahlen sind, einerseits für Chlor- und Bromverbindungen, anderseits für Brom- und Jodverbindungen unter einander gut überein und kommen ihrer Grösse nach uns wahrscheinlich vor.

Aus Tabelle 12 geht hervor, dass Verbindungen mit niedrigerem Bromgehalt und hoher Verbrennungswärme auch ohne Paraffinzusatz verbrannt werden können. — Vgl die sehr konstanten Werte der reduzierten Brommenge in der letzten Kolumne!

Zuletzt wurde für Chlorverbindungen ein Vergleich zwischen Verbrennungen nach der Sch.-methode, Qw-methode und Rotationsmethode gemacht. Für die erstgenannten Methoden findet man die Ziffern schon oben in Abteil. I, für die letztgenannte scheint es uns überflüssig die Originalziffern hier anzuführen;

Tabelle 13.

Substanz	Qw-methode	Sch-methode	Rot.-methode
o-Chlorbenzoesäure . .	4723[1]		4724
m- » . .	4685[1]	4678	
p-Dichlorbenzol . . .	4773[1]	4770	4772
1,2,4-Trichlorbenzol . .	3693	3681	3690

[1] Bestimmung von K. J. Karlsson-Karrman.

wir geben nur die Mittelwerte an: die Mengen Paraffinöl u. s. w. stimmen mit den bei den Schaukelversuchen benutzten überein. — Die mittlere Genauigkeit der Rot-methode dürfte etwa derjenigen der Q_w-methode entsprechen.

Die vorzügliche Übereinstimmung zwischen Q_w- und Rot-resultaten zeigt, dass *beide* Methoden von systematischen Fehlern frei sein müssen. Die Sch.-methode gibt dagegen wahrscheinlich bei Substanzen mit sehr hohem Chlorgehalt etwas zu niedrige Verbrennungswärmen.

Zu dieser Arbeit haben einerseits „Svenska Sockerfabriks A.B." andererseits das Nobelkomitee für Chemie freundlichst Unterstützung gegeben, wofür der eine von uns (Smith) bestens danken möchte.

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Quantitative Adsorption Analysis of Some Amino Acid and Peptide Mixtures on Active Carbon.

(Preliminary Report.)

By Arne Tiselius.

From the Institute of Physical Chemistry, University of Uppsala.

In a number of earlier papers by the author and Claesson (1, 2) a method for adsorption analysis has been described which is particularly well suited for the quantitative observation of the adsorption and elution processes in solutions passing through a column. The method is based upon continuous measurements of the concentration of the solution leaving the column, and is thus independent of the colour of the adsorbent or that of the substances to be adsorbed. Some applications of the method for the separation of carbohydrates and lipids have also been described in earlier communications (3, 4, 5). Determinations of the adsorption by front analysis on solutions of a number of amino acids and peptides when active carbon is used as an adsorbent (Table 1, see 6) have demonstrated that the individual differences in adsorption capacity between these substances are very marked, so that a quantitative separation in many cases ought to be possible. The present paper describes some further experiments to this end.

For the problem of structure determinations on proteins, amino acid analyses are naturally of the utmost importance. There is a general opinion among protein chemists that the classical methods do not satisfy modern requirements as to accuracy and the amount of material required. This is of course particularly true of the proteins and peptides with biological activity, of which only small quantities are usually available for analysis. For studying the sequence of amino acids in a protein polypeptide chain and particularly for test-

Table 1. Retardation Volumes in the Adsorption of Some Amino Acids and Peptides on Active Carbon (*Carbo Activ Schering*). 0.5 per cent aqueous solutions.

Substance	Ret. vol. ml/g carbon	Substance	Ret. vol. ml/g carbon
Alanine	0.8	Glycyl-glycine	3.5
Hydroxyproline	2.0	Leucyl-glycine	18.2
Proline	2.5	Leucyl-glycyl-glycine	29.8
Valine	3.2	Glycyl-alanine	4.0
Leucine	7.7	Valyl-alanine	22.0
Isoleucine	9.2	Alanyl-leucyl-glycine	34.4
Methionine	12.4	Glycyl-leucyl-alanine	42.5
Histidine	15.0	Glycyl-leucyl-glycine	38.0
Arginine	40.4		
Tryptophane	76.5		
Phenylalanine	62.5		

ing the Bergmann-Niemann hypothesis concerning the periodical arrangement of amino acid residues in such chains, the most direct information should be provided if one could isolate fragments of the chain and determine their structure. Attempts in this direction have been made by many authors (7, 8). A generally applicable method of isolating peptides from protein hydrolysates should be of great value to workers in this field.

During the last few years a considerable number of papers on the application of adsorption methods to amino acid analysis have appeared (for a recent review see a paper by Wieland (9) and further a number of papers by Martin, Gordon and Synge (10). By using exchange adsorbents, like aluminium oxide, permutites, organolites and active clay preparations, it is now possible to divide quantitatively an amino acid mixture into three fractions containing the dicarboxylic mono-amino, the diamino-monocarboxylic and the monoamino-monocarboxylic acids respectively. It is also possible with these adsorbents to subdivide the two first-mentioned fractions into aspartic and glutamic acids and arginine, lysine and histidine respectively. The neutral amino acids do not show any specific adsorption on exchange adsorbents. In ethyl alcohol solution, or in aqueous solution after treatment with formalin (9) their electrochemical character may be modified, however, so that a certain fractionation may be obtained on exchange adsorbents with these

amino acids also. Gordon, Martin and Synge use acetylated amino acids in organic solvents with a moist silica gel as adsorbent (10). By impregnating the silica gel with a suitable indicator they are able to observe directly the migration of the various components in their column and have been able to separate quantitatively several amino acids. It appears probable that the best results in adsorption analysis of amino acid mixtures will be obtained by a successive application of different adsorbents. From this point of view a further investigation of the possibilities offered by adsorption on carbon has seemed worth while, especially as such work is necessary as a prelude to an investigation of the application of this adsorbent to the problem of peptide separation.

The observation (see Table 1 above) that tyrosine, tryptophane and phenylalanine are adsorbed much more strongly than other amino acids on carbon has been utilized by Schramm and Primosigh (11) as a quantitative separation method. Following a suggestion of the author (6) they used cyanide-poisoned carbon to eliminate the risk of catalytic oxidation of the amino acids, which for some samples of carbon may be a serious source of error. Similar experiments have been made by Wachtel and Cassidy (12).

Application of the author's method, however, makes a separation possible also in such cases where the differences in adsorption are much smaller than in the last-mentioned case, as the following examples will demonstrate.

The simplest form of adsorption analysis, which we have called front analysis as only the partial separation taking place at the adsorption front in the column is observed, is sometimes very useful. In the ideal case of mutually independent adsorption for the components of a mixture, the differences in heights of successive steps correspond to the concentrations in the original sample. Such is the case only when the components to be determined are weakly adsorbed or the concentrations are very low. For amino acids this procedure may be applied to determinations of glycine and alanine in the presence of other amino acids. Glycine and alanine may even be separated from each other but this requires very large adsorption columns. An example of this type of experiment

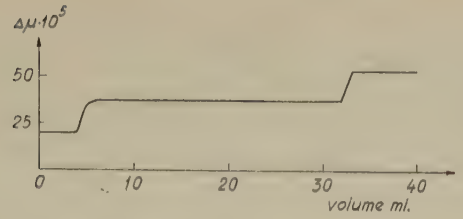

Fig. 1. Front analysis of a mixture of alanine and leucine.

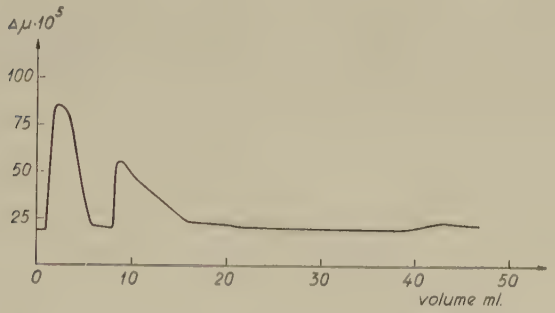

Fig. 2. Elution analysis of a mixture of alanine, valine and leucine.

is given in Fig. 1, where a mixture of alanine (0.159 mg.N/ml.) and leucine (0.104 mg. N/ml.) on 1.5 g. *Norit P 3 Spezial* (active carbon) gives a two-step curve in which the first step is pure alanine, which on analysis gives a concentration of 0.161 mg.N/ml. Such analyses have been tried with alanine or glycine mixed with valine, methionine, tryptophane and phenol with equally good results. The procedure requires somewhat larger quantities than those described below, although quite dilute solutions (0.1 per cent) may be used.

In the front analysis the original solution flows through the column until all components have appeared. If "development" is used as in ordinary chromatography, only a few millilitres of the sample are pressed into the column and forced to migrate through by elution or displacement with a suitable solution. By this procedure a complete separation of the mixture into its components may be obtained. A typical elution experiment is demonstrated in Fig. 2 which shows the analysis of a 3 ml. sample containing alanine (1.55 mg.N), valine (1.06 mg.N) and leucine (0.97 mg.N) on a column of 1.5 g. *Carboraffin C.* Only water was used for the elution and it is

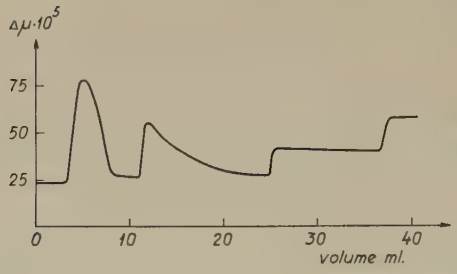

Fig. 3 a. Displacement analysis of a mixture of valine, leucine and methionine, with 0.5 per cent ethyl acetate as displacing solution.

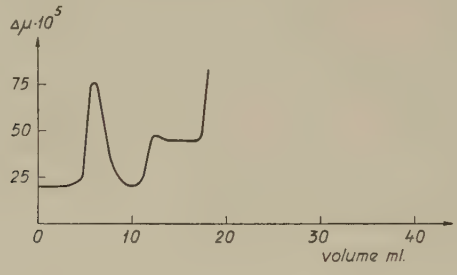

Fig. 3 b. Displacement analysis of a mixture of valine and leucine, with 5 per cent phenol as displacing solution.

seen from the diagram that the leucine, which is most strongly adsorbed, shows a marked "tailing". The analysis of the three portions gave 1.59, 1.05 and 0.82 mg.N respectively, confirming that leucine is not quantitatively eluted by water. Fig. 3 a—b gives an example of the application of what the author has called displacement development, in which a strongly adsorbed substance displaces the components, giving rise to a stationary concentration distribution in which each component adjusts itself to a characteristic concentration (3, 13). Fig. 3 a demonstrates this case for a mixture of valine (1.28 mg.N), leucine (1.06 mg.N) and methionine (0.95 mg.N). The sample has been displaced through the column by a 0.5 per cent solution of ethyl acetate. Evidently, with the comparatively short column used (1.5 g. *Carboraffin C*) valine and leucine have not yet reached a stationary concentration and therefore appear as more or less distinct peaks, whereas methionine, which is most strongly adsorbed and therefore appears to the right in the

diagram, has reached the stationary state. The three portions gave 1.30, 1.02 and 0.84 mg.N respectively. The remaining methionine nitrogen could, however, be washed out from the column with 5 per cent ethyl acetate (total yield 0.95 mg.N). The 0 5 per cent ethyl acetate evidently does not displace the methionine completely. The leucine, however, is in this case displaced quantitatively by the succeeding methionine. The diagram now discussed is really a mixture of a displacement and an elution diagram, the valine being eluted and the methionine displaced. A pure displacement diagram is shown in Fig. 3 b, obtained by choosing a high concentration for the displacement developer (in this case 5 per cent phenol). The column was 1.5 g. *Carboraffin C.* The two steps are valine (1.28 mg.N) and leucine (0.96 mg.N). Analysis gives 1.35 mg.N and 0.88 mg.N. The errors are probably due to the difficulty of changing the collection vessel at the exact boundary between the two amino acids.

The above examples have purposely been chosen among those amino acids which are difficult to separate quantitatively by other methods. Other mixtures are much easier to analyse also by this method. The method is convenient, requires only small amounts of material, but is perhaps not of very high accuracy. The author has, however, not concentrated upon the improvement of the accuracy, as these experiments were merely intended to give a basis for further experiments with peptides. Waldschmidt-Leitz and Turba (14, 15) made the first really successful fractionation of peptides by adsorption when they succeeded in obtaining several distinct components from a clupein hydrolysate in a column of *Filtrol-Neutrol.*

According to Table 1, peptides are adsorbed more strongly than their component amino acids, and it should be possible to separate several peptides from each other just as effectively as the amino acids. Several combinations of di- and tripeptides have been tried. Fig. 4 shows an elution analysis of 1 ml. solution containing alanyl-glycine (1.95 mg.N) and alanyl-glycyl-glycine (2.03 mg.N). It is seen that both peptides appear as separate peaks in the diagram, as the adsorption is comparatively weak. Only water was used for the elution with an adsorption column of 3.0 g. *Carboraffin C.* Kjeldahl nitrogen

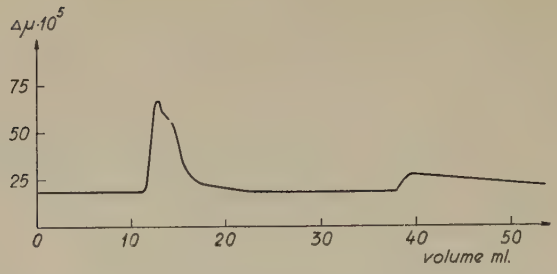

Fig. 4. Elution analysis of a mixture of alanyl-glycine and alanyl-glycyl-glycine.

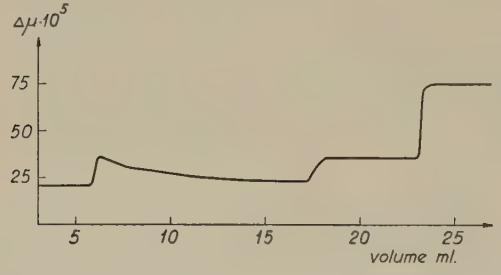

Fig. 5. Displacement analysis of a mixture of leucyl-glycine and leucyl-glycyl-glycine, with 0.25 per cent phenol as displacing solution.

analysis of the isolated fractions gave 1.88 mg.N for the alanyl-glycine and 1.98 mg.N for the alanyl-glycyl-glycine. There are thus some losses, particularly of the tripeptide. Fig. 5 shows a displacement analysis of a mixture of leucyl-glycine (0.75 mg.N/ml.) and leucyl-glycyl-glycine (0.85 mg.N/ml.). These peptides cannot be eluted with water on account of their comparatively strong adsorption (see Table 1 above). In this case only 0.25 g. *Carboraffin C* was used with 0.25 per cent phenol as displacing solution. The analysis gave 0.77 and 0 80 mg.N respectively.

Judging from these and other experiments it is possible to differentiate and separate the lower peptides by adsorption on carbon. For peptides showing strong adsorption (retardation volumes larger than about 20 ml. per g. carbon, see Table 1) considerable losses also occur when the displacement method is used. Similar difficulties were encountered in the work of Tiselius and Hahn (4) on the separation of higher saccharides.

Here the losses could be largely eliminated by using very efficient displacing substances (ephedrine) and by reducing the activity of the carbon by a preliminary treatment with a dilute solution of the displacing substance. Ephedrine is a much more efficient displacer than phenol for peptides also but has the drawback of interfering with the nitrogen analysis. Some experiments were made in which a layer of an exchange adsorbent, *Filtrol-Neutrol* (obtained from the firm *Herman Bensmann*, Bremen), was packed in the bottom of the adsorption cell, below the carbon column. The *Filtrol* layer selectively adsorbs the ephedrin, and thus a gap is obtained between the leucyl-glycyl-glycine layer and the subsequent ephedrine front. In this way the losses were reduced considerably, but in some cases still amounted to 5 per cent. Other displacing substances are now being tried.

Another way of attacking this problem which seems more promising is also being tried, namely to use carbon preparations which have been partly inactivated, so that the adsorption affinity for the higher peptides may be reduced.

For peptides containing diamino acids exchange adsorbents are probably more favourable, as is evident from the experiments by Waldschmidt-Leitz and Turba on the isolation of digestion products from clupein hydrolysates.

Summary.

Some experiments are described in which the new adsorption analysis method is applied to the separation of monoamino-monocarboxylic acids and some peptides of the same type using an active carbon as adsorbent. Quantitative separations are possible with the amino acids and with those peptides which show low adsorption affinity for carbon. With the higher peptides losses occur and some methods of eliminating this difficulty are discussed.

This investigation has been financially supported by a grant from "Svenska Nationalföreningen mot Tuberkulos".

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On the Chemistry of Sulphite Cellulose Cooking.

By Sixten Ulfsparre.

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The manufacture of sulphite cellulose is based upon the capacity of lignin to react with acid sulphites and sulphurous acid, whereby it is changed into a water-soluble form.

Tilghman (1) in America, was the first to obtain a patent on the digestion of wood to sulphite pulp. C. D. Ekman and A. Mitscherlich first solved the problem technically. They all worked empirically. Investigations with respect to the reactions taking place during the digestion of wood with sulphite cooking acid were in fact not published until 1890. A Norwegian, Pedersen (2), examined sulphite waste liquor and found that the greater part of the sulphur content of the liquor was organically combined.

The chemical composition of the wood substance had already been an interesting object of research during the first decades of the 19th century. In 1819 Braconnot (3) thus found that treating white beechwood with strong sulphuric acid resulted in high yields of water-soluble carbohydrates.

At that time it was believed that wood was built up from a homogeneous material, but the work of Payen (4) proved this conception to be erroneous. Payen treated samples of wood with nitric acid, alkali, alcohol and ether, and constantly obtained a residue corresponding to the formula $C_6H_{10}O_5$ which he considered to be indentical with cellulose. The substance dissolved during the treatment was called "incrustants" which formed a mechanical protection of the cellulose in the cell wall. Schulze (5) showed that the cell structure of the cellulose was still intact upon the removal of the incrustants by

oxidation with potassium chlorate and nitric acid, and that the formation of wood was therefore caused by the incrusting substance, which he termed lignin.

Sulphonation of Lignin.

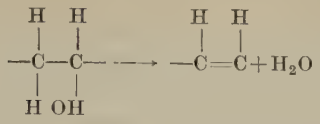
By the transformation of the incrusting substance into a water-soluble form in the sulphite waste liquor, a material was obtained which allowed a closer study of the lignin. It was assumed that by this relatively mild treatment, the native lignin was not changed, or only very slightly so. Lignin sulphonic acid was isolated for the first time by Lindsey and Tollens (6), by precipitation with lead acetate. By decomposing the lead salt with sulphuric acid and precipitating in alcohol, they obtained a substance corresponding to the formula $C_{26}H_{30}SO_{12}$. By distillation with hydroiodic acid, it was shown that the substance contained two methoxyl groups. The sulphur was combined as SO_3H.

From this time on, the lignin sulphonic acid has been used and recommended as a basic material for lignin studies, and numerous investigators have tried to solve the secret of lignin from this starting point. No doubt this work has to a great extent enriched our knowledge concerning the reactions which take place during the sulphite cooking process.

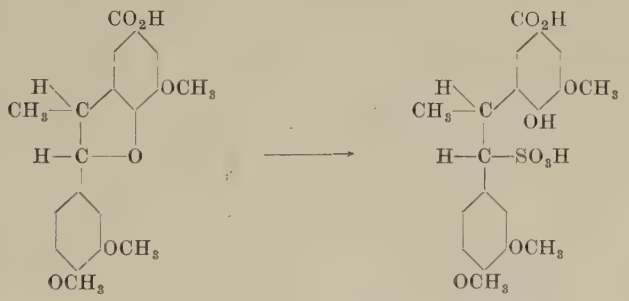
The theory of Klason (7), which long remained unchallenged, assumed that the transformation of lignin into a soluble lignin sulphonic acid took place through the addition of sulphite to an ethylenic linkage in the lignin molecule, as follows

$$\begin{array}{l} -CH \\ \quad \| \\ -CH \end{array} + SO_2 + H_2O \rightarrow \begin{array}{l} -CH_2 \\ \quad | \\ -CHSO_3H \end{array}$$

Freudenberg, Belz and Niemann (8) found, however, that lignin reacted with bromine, forming one equivalent of hydrogen bromide. The existence of double bonds could be shown only to a slight extent by treatment with lead tetraacetate. Freudenberg therefore raised the question as to whether an ethylenic linkage could result from the expulsion of water in the lignin molecule



This would mean the loss of one methylatable hydroxyl group, but Hägglund and Carlson (10) have shown that this does not occur. Sulphonation by the formation of ethers can only take place in one half of the lignin molecule. If the number of methylatable hydroxyl groups is to remain constant, the other half of the molecule must be sulphonated with the formation of a new hydroxyl group, i. e., by the rupture of an oxygen linkage, as in the case of "Erdtman's acid". Freudenberg demonstrates the sulphonation of lignin as follows by means of his model substance:



On account of the similarity between the reactions of lignin with thioglycolic acid and with sulphurous acid, Holmberg (11) in 1935 proposed the following scheme for the sulphonation of lignin

$$—C \cdot OH + H \cdot SO_3H \rightarrow —C \cdot SO_3H + H_2O$$

He refers to the fact that α-phenethyl alcohol reacts with a bisulphite solution at 130° with the formation of sulphonic acid (12):

$$C_6H_5 \cdot CH(OH) \cdot CH_3 + NaHSO_3 \rightarrow C_6H_5 \cdot CH(SO_3Na) \cdot CH_3 + H_2O$$

Unity of conception as to the details of the sulphonation reactions would require a much broader knowledge in regard to the molecular structure of the lignin substance.

The Dissolution of the Lignin Sulphonic Acid.

The sulphite cooking process may be divided into two stages, viz., sulphonation in the solid phase and the dissolution of the lignin sulphonic acid thus formed. The hydrogen ion concentration plays a rôle in both stages. Hägglund and Johnson (13) showed that a decrease in pH, while other experimental conditions remained constant, caused an increased sulphur content of the wood residue. The sulphonation proceeds relatively rapidly until a degree of sulphonation is reached which corresponds to 1 sulphur per 40 carbon in the lignin molecule, but the velocity of reaction later decreases when the sulphonation increases to 1 sulphur per 20 carbon. When the degree of sulphonation corresponds to a sulphur content of 1 S per 40 C or more in the lignin molecule, it is possible to transform the solid lignin sulphonic acid into a water-soluble form by hydrolysis. Hägglund (14) has shown, by cooking sulphonated wood with buffer solutions, that the velocity of dissolution is directly proportional to the hydrogen ion concentration. In this connection, great interest has been attached to the observation of Kullgren (15) that the solid lignin sulphonic acid could be dissolved by means of pure water or alcohol, if the sulphonated wood was first treated with dilute acid, which causes an exchange of the metal cations in the solid acid against hydrogen. Hägglund and Johnson (16) proved that the dissolution of the acid by pure water is in any case a form of hydrolysis, catalysed by hydrogen ions. Their investigations showed that the solid acid was dissociated to a great extent into ions and that it reacted as a strong acid of high concentration. Strong sulphite pulp should thus definitely be regarded as a permutoid. This question has been examined in a series of investigations carried out by Kullgren and Du Rietz (17).

The catalytic effect of the hydrogen ions on de dissolution of the solid lignin sulphonic acid has been shown by Hägglund and Sävö (18). They determined the reaction constant for the dissolution at different conditions of acidity. The reaction was bimolecular until about 70 per cent of the lignin was dissolved. The velocity then decreased, probably owing

to the condensation of the lignin sulphonic acid to larger units.

The dissolution of lignin during sulphite cooking naturally also depends upon the velocity of the sulphonation. This is governed by the concentration of the hydrogen ions, as well as the bisulphite ions, the sulphonation being more rapid at higher concentrations. Maass (19) and co-workers have devoted much attention to studies of the reaction of dissolution. They consider that the product of the hydrogen and the bisulphite ion concentrations is the controlling factor, and on the basis of this assumption have tried to formulate the dissolution of the lignin mathematically. It has been pointed out above, however, that the sulphonation and the dissolution processes are bound together in a manner which presumably makes it impossible to set up any formal satisfying the velocity of reaction in sulphite cooking.

Properties of the Dissolved Lignin Sulphonic Acid.

As already mentioned, the dissolved lignin sulphonic acid could be isolated as a basic lead salt or by precipitation with alcohol. Klason (20) found that approximately one-half of the dissolved quantity could be salted out by means of $CaCl_2$, while Melander (21) obtained 37 per cent of the amount of lignin, by using NaCl. From the fraction thus salted out, Klason prepared a barium salt with the composition $C_{40}H_{44}O_{17}S_2Ba$. The methoxyl content was 11.5 per cent, which corresponds to one methoxyl group for each C_{10}-residue. Procter and Hirst (22) found that it was possible to precipitate the lignin sulphonic acid with certain aromatic amines. Precipitations obtained by means of α- and β-naphthylamine were most generally investigated. In a comprehensive series of investigations Klason (23) studied the naphthylamine compounds obtained. The waste liquors examined by him constantly yielded lignin sulphonic acids, two-thirds of which could be precipitated, while one-third did not precipitate. The part that precipitated he called α-acid, and the remainder β-acid. It was his opinion that the lignin already occurred in the wood as α-lignin and β-lignin. The difference between these compounds was revealed

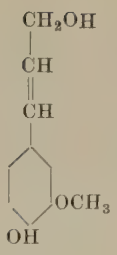
by the aldehydic nature of the α-lignin, in contrast to the presence of a carboxyl group in the β-lignin (24). Hägglund (25), however, found that the amount of precipitate obtained depended upon the method used in digesting the wood. On cooking with SO_2-water alone it was possible to precipitate almost the entire amount of dissolved lignin sulphonic acid with naphthylamine. This was also possible if the sulphite waste liquor was dialysed before the precipitation. This demonstrated clearly that the degree of precipitation was a function of the molecular size of the lignin sulphonic acid. Later, Erdtman (26) compared different bases as precipitants in a comprehensive series of investigations. He found that 4,4′-bis-dimethyl-amino-diphenylmethane was a suitable reagent for the isolation of the high molecular fraction in sulphite waste liquors. The low molecular fraction of the β-lignin sulphonic acid was isolated by Hägglund and Johnson (27) as a barium salt by precipitation with alcohol after the removal of the α-acid. The precipitate thus obtained was purified by the removal of salts of carboxylic acids by a fractional treatment with sulphuric acid. When the resulting acid was analysed, it showed a higher content of sulphur, and a lower content of methoxyl than the α-acid. It also reduced Fehling's solution considerably. According to Erdtman (28), it is probable that the low molecular fraction is heterogeneous, consisting of a mixture of lignin sulphonic acid and sulphonated sugars.

On the basis of his investigations of the lignin sulphonic acids, Klason (29) proposed at an early date his well-known hypothesis suggesting that the lignin was built up of coniferyl and hydroxyconiferyl alcohols and this theory he expounded and fought for in a long series of papers. In 1916 he published an investigation (30) in which he suggested the following reaction equation for the α-acid:

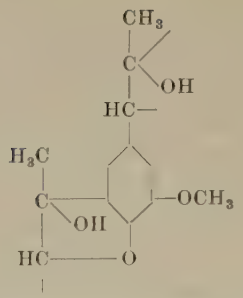
$$\underset{\substack{\text{Coniferyl}\\\text{alcohol}}}{C_{10}H_{12}O_3} + 3\underset{\substack{\text{Hydroxy-}\\\text{coniferyl}\\\text{alcohol}}}{C_{10}H_{12}O_4} + Ca(HSO_3)_2 \rightarrow \underset{\substack{\text{Calcium salt of}\\\text{lignin sulphonic acid}}}{C_{40}H_{44}O_{18}S_2Ca} + 3H_2O$$

With regard to the β-acid molecule he assumed that it contained one molecule of caffeic acid $C_9H_8O_4$ besides one molecule each of coniferyl alcohol and hydroxyconiferyl alcohol.

The presence of aromatic groups in the lignin was a matter of controversy for a long period. At an early stage it was known, of course, that the decomposition of the lignin molecule by means of alkaline fusion resulted in small quantities of aromatic substances such as pyrocatechol, protocatechuic acid and vanillic acid (31), but this was not considered sufficient evidence. As early as 1904, Grafe (32) succeeded in isolating small amounts of vanillin from sulphite waste liquor, which was heated in the presence of lime to 180° C. This interesting reaction has later been studied by a great number of lignin research workers. It is well known that the comprehensive research of Tomlinson and Hibbert 33) (cf. also (34)) into this problem has led to the manufacture of vanilla from sulphite waste liquor on a technical scale. According to Freudenberg, Lautsch and Engler (35) it is possible to obtain very high yields of vanilla by pressure heating in an alkaline solution at 160° C in the presence of nitrobenzene. Applied to lignin sulphonic acid this method yielded 20 per cent vanilla while spruce-wood yielded 25 per cent with respect to the lignin content. Freudenberg and co-workers (36) have also been able to isolate a number of aromatic groups in high yields by fusion with KOH for short periods at 210° followed by methylation and oxidation of the resulting reaction products; in this way they have accounted for the greater part of the lignin molecule as consisting of aromatic groups. Measurements of the selective absorption of ultra-violet rays (37) by different lignin compounds have also served as an evidence in favour of the aromatic nature of the lignin. The most modern investigation in this respect has been carried out by Lange (38) who measured the absorption of *native* lignin in sections of spruce wood by the use of an ultra-violet microscope. The structure of lignin cannot as yet be considered quite clear in all details but particularly thanks to the work of Freudenberg and Hibbert (for summary see 39) on this subject it has been definitely proved that the basic component is phenyl propane, probably arranged in the same manner as guaiacyl propane in coniferyl alcohol:



Coniferyl alcohol



Structural formula for lignin suggested by FREUDENBERG

This is essentially a confirmation of the hypothesis of KLASON, although he never succeeded in producing sufficient evidence to prove his point.

The Dissolution of the Wood Polyoses during Sulphite Cooking.

SCHULZE (40) assigned the term *hemicellulose* to those water-soluble polysaccharides which could be hydrolysed with dilute mineral acid leaving the cellulose intact. Later it became clear that no such definite line could be drawn between the cellulose and the rest of the polysaccharides in the wood. STAUDINGER and REINECKE (41) therefore introduced the term *wood polyoses* for the latter.

Depending upon the conditions of cooking, a greater or smaller part of the wood polyoses goes into solution. The composition of the dissolved carbohydrates remained an uncertain factor for some time. The presence of pentose and mannose was early shown (42). KLASON (43) reported in 1917 that about one-half of the reducing substances consisted of glucose. In sulphite cooking the wood polyoses are hydrolyzed to simple sugars. The presence of polymerised carbohydrates in sulphite waste liquor has not been definitely established.

For a long time it was held that the considerable variations in the content of reducing substance was due to some destruction of the sugar (mummification) in a manner similar to that taking place when sugar solutions are heated under pressure in the presence of mineral acids. In view of the relatively

low acidity prevailing in a sulphite cook, this explanation was not reasonable. By investigations of the sulphonation of lignin Hägglund and Johnson (44) were able to show that black cooks would result very soon if the sulphonation took place in the presence of glucose. The content of glucose decreased simultaneously. This was shown to depend upon the fact that the bisulphite ions oxidised the sugar to aldonic acids with the simultaneous formation of thiosulphate (45):

$$2HSO_3' + 2C_6H_{12}O_6 \rightarrow 2C_6H_{12}O_7 + S_2O_3'' + H_2O$$

Hägglund and Johnson also succeeded in showing the presence of xylonic acid in sulphite waste liquor and they isolated mannonic acid in the form of crystalline brucine salts. These investigations made clear the relation between the yield of sugar and the concentration of sulphite in the cooking acid. The amount of sugar oxidised to aldonic acids increases with an increasing concentration of sulphite in the cooking liquor. The danger of re-using liquor rich in sugar also became evident (46). The increased formation of thiosulphate accelerates the decomposition of the sulphite in the same manner as selenium.

When cooking is performed with high concentrations of sulphite in the acid, a small amount of sugar sulphonic acids is also formed. As mentioned before, these are probably a constituent of the low-molecular fraction obtained in the isolation of lignin sulphonic acid. Hägglund, Heiwinkel and Bergek (47) have studied the formation of these hitherto unknown compounds more thoroughly and have found them to be of different types. One group were stable sulphonic acids, while another consisted of unstable sulphonic acids which could be regenerated into sugar and sulphite. When strong sulphite pulp is cooked under certain conditions a sugar-sulphite compound may be formed, which is stable at pH-values between 4 and 7. This compound has a pronounced inhibitory action upon the fermentation process and thus causes a considerably decreased yield in the production of alcohol.

With the continued improvement of the quantitative methods for the determination of sugar, it also became possible to determine more exactly the different types of sugar in the

sulphite liquor as well as the different wood polyoses remaining in the sulphate pulp.

Data obtained by Hägglund and co-workers regarding the composition of the wood substance in Swedish spruce (in per cent) may be given as a summary of this chapter:

	Cellulosic	Easily hydrolysed	
Cellulose			41.0
Wood polyoses built up of			
Mannose	3.8	6.7	10.5
Glucose	—	6.9	6.9
Xylose	2.6	5.3	7.9
Fructose	1.1	0.1	1.2
Galactose	—	1.0	1.0
Lignin			27.8
Acetyl			1.4
Resin, ash, protein etc.			2.3
			100.0

Easily hydrolysed wood polyoses comprise the fraction that is dissolved in normal cooking of strong sulphite pulp (Roe number = 7). The hydrolysis is considerably stronger in the cooking of rayon pulp (Roe number = 1) and the distribution of the wood components (in per cent of the wood substance) in this case will be approximately as follows:

	In pulp	In waste liquor
Cellulose	39.5	1.5 (glucose)
Wood polyoses		
Mannose	0.9	9.6
Glucose	—	6.9
Xylose	0.5	7.4
Fructose	0.4	0.8
Galactose	—	1.0
Lignin	0.4	27.4
Acetyl	—	1.4
Resin etc.	0.6	1.7

Wood Cellulose.

Tollens (48) defines cellulose as a substance present in the cell walls of plants with the formula $C_6H_{10}O_5$, built up of a polymerised anhydride of *d*-glucose and yielding cellobiose upon acetylation.

Different methods have been used to determine the cellulose content of wood. An early method used was one suggested by Cross and Bevan (49) by which wood flour was treated with a 1 per cent solution of NaOH, chlorine and a 2 per cent solution of Na_2SO_3 and finally bleached with a 0.1 per cent solution of $KMnO_4$. Klason (50) defined wood cellulose as the residue of carbohydrates which resulted on treating the wood material at 98° C with a solution containing 13 grams of free and 37 grams of combined SO_2 per litre. The time of treatment should be at least 10 days and the yield of cellulose varies around 57 per cent.

These methods, original or modified, do not yield pure cellulose. In order to ascertain the true content of cellulose it is necessary to determine the composition of the polyoses in the residue. Hägglund (51) carried out exhaustive analyses of sulphite pulp prepared in different ways and found that the average cellulose content of Swedish spruce-wood amounted to 41 per cent. Staudinger and Husemann (52) arrived at the same result by removing the lignin by means of chlorine dioxide or an acidified solution of $NaClO_2$ followed by a treatment of the residue with a 10 per cent solution of NaOH in an atmosphere of nitrogen.

Until recently, cotton cellulose has been practically the only basic material studied in determining the chemical and physical properties of cellulose. The opinion has often been voiced that the character of wood cellulose is different from that of cotton cellulose. Sherrard and Blanco (53), for instance, consider the spruce cellulose to be built up of pentose and hexose residues, thus being a mixture of polysaccharides.

Herzog and Jancke (54) have found, however, that cotton and wood cellulose produce identical interference figures when examined with X-rays according to the method devised by Debye and Scherrer.

Staudinger and Husemann (52) determined the average degree of polymerisation of different wood celluloses and found values between 960 and 1 200. Klauditz (55) reports considerably higher values, obtained by isolating the cellulose either by means of chlorine and alkali, or by chlorine dioxide and pyridine followed by an additional treatment with 5 per cent

sodium hydroxide. Cellulose isolated by means of chlorine showed DP 1 700—1 780, while samples treated with chlorine dioxide gave DP 1 910—1 970. Dolmetsch and Reinecke (56) determined the polymolecularity of different wood celluloses by fractional dissolution of the products obtained after nitration, and viscosimetric determinations of the chain length. They found that wood cellulose was more polydisperse than cotton cellulose.

Atchison (57) nitrated holo-cellulose and sulphite, sulphate, and alkali pulps and then determined the specific viscosity according to Staudinger. By fractionation he found that the carbohydrate fraction of the wood was very heterogeneous, but that an equalisation took place during the treatment, caused by decomposition and dissolution of low-molecular fractions, resulting in an increased DP. This equalisation is more pronounced in sulphate cooking, a fact which Atchison claims to be the reason for the greater strength of sulphate pulps. The polydispersity increases when the pulps are bleached.

Svedberg (58) and recently Gralén (59) have described reliable methods based upon measurements of sedimentation and diffusion by which it is possible to arrive at the degree of polymerisation and the polydispersity. Gralén found, for instance, that cellulose extracted from wood by means of cuprammonium hydroxide had an average molecular weight of minimum 800 000 (DP 5 000). Gralen and Ränby (p. 274, this book), showed by nitration of wood from an early stage of the sulphite process that the molecular weight of wood cellulose in its native state is still higher. Gralén (59) states that there is a tendency towards increase in the polydispersity with decreasing molecular weight.

The Significance of the Final Temperature and the Lime Content in the Cooking of Rayon Pulp.

Earlier investigations concerning the effect of the maximum temperature and the lime content upon the cooking procedure have chiefly dealt with the manufacture of pulp to be used in paper and the yields have been related to the degree of delignification. With regard to the cooking temperature sche-

dule, Hägglund (60) found that pulp obtained at a maximum temperature of 120° C as well as 135° C was easily defibrated, and that the resulting yield was about 55 per cent at a lignin content of 7—8 per cent. At still higher temperatures the dissolution proceeded so rapidly as to make it difficult to determine exactly when the cook was finished, the reason being that an increase of the maximum temperature by 10° C doubled the velocity of reaction.

In cooking experiments using acids of varying lime contents Hägglund (61) found that the yield of pulp, containing the identical amount of lignin, increased with an increased content of lime. This has been confirmed by Bergman (62) and Maass (63).

Eastwood (64) claims that the yield of pulp is independent of the final temperature but that the temperature schedule has a decided bearing upon the strength and uniformity of the pulp. Mc Govern and Chidester (65), however, found that the yield decreased by 0.5 per cent when the final temperature was increased by 10° C in the range 130—150° C. With regard to the manufacture of rayon pulp Hüter (66) is of the opinion that the time gained by a forced cooking schedule is sufficient compensation for the loss in yield and the resulting lower content of α-cellulose.

Okada and Hayakawa (67) have reported some results from attempts to follow the change in the relative viscosity for different methods of cooking and they point out the interdependence of the colour of the cooking liquor and the viscosity. They also state that the α-cellulose content passes through a maximum in the later stages of the cook. Johansson (68) also determined the change in viscosity in the course of cooking and found that the viscosity curve was essentially constant. His investigations applied to cooking with low contents of the base. He reports the existence of a certain parallel between the colour of the liquor, the yield of pulp and the viscosity.

Jayme and Groegaard (69) have investigated the possibilities of a continuous cooking process. The high temperature required in such methods of cooking they held to be of advantage since the α-cellulose content of the pulp increased.

Table

Temperature	130° C			135° C		
Viscosity	Yield	α-content	α-yield	Yield	α-content	α-yield
m P	%	%	%	%	%	%
600	42.6	88.7	38.0	42.9	89.0	38.8
500	41.8	88.6	37.6	42.8	89.0	37.9
400	40.8	88.5	36.4	41.2	89.1	36.8
300	38.8	87.6	33.0	39.4	89.9	35.3
200	—	—	—	36.0	89.0	32.3
Sugar g/l m, v,	35.0			36.6		

At a maximum temperature of 170° C, they obtained an α-content of almost 92 per cent based on the bleached product; the lignin content of the unbleached pulp, however, was no less than 5 per cent. The autoclaves were heated rapidly to 170° C and the total cooking time was only 68—76 minutes, allowing 15 minutes at 170° C.

In the manufacture of pulp for paper-making the yield of the pure cellulose is generally 100 per cent. Thus it is clear that in cooking down to the same lignin content, higher yields of pulp are reflected in correspondingly higher contents of wood polyoses. In rayon pulp manufacture, on the other hand, the aim of the digestion is to reduce the content of wood polyoses as much as possible, at the same time producing a pulp of a definite and relatively low viscosity. During the later stages of the cook the dissolution of lignin is slight but the decreases in the yield and viscosity are more or less pronounced, in accordance with the cooking conditions. A clearer conception of the reactions in the cooking of rayon pulp may thus be obtained by relating the yields of pulp to the viscosity rather than to the usual tests expressing the lignin content.

The fact that the final stages of the cook are characterised by a decreasing yield while the lignin content remains fairly constant, provides evidence for the obvious fact that the carbohydrates are being hydrolysed and dissolved. Should the wood

140° C			145° C			150° C		
Yield	α-content	α-yield	Yield	α-content	α-yield	Yield	α-content	α-yield
%	%	%	%	%	%	%	%	%
45.0	89.8	40.7	45.3	89.8	40.6	47.1	89.8	42.3
44.3	89.4	40.1	44.6	90.1	40.3	46.8	89.9	42.0
43.4	89.8	39.5	43.9	90.3	39.7	46.2	90.0	41.6
42.2	90.3	38.4	42.8	90.4	38.9	44.4	90.1	40.0
40.7	90.3	37.0	41.2	90.3	37.5	43.6	90.2	39.2
	38.0			39.9			40.5	

polyoses then be attacked more rapidly than the cellulose proper, a higher α-content would result.

The effect of different cooking conditions upon the degradation of the cellulose and the wood polyoses is, therefore, of very great interest to the producers of rayon pulp. The following summary of cooking experiments carried out at the Domsjö sulphite mill in 1938—1940 shows the importance of the final temperature and the lime content in regard to the yield of pulp and α-cellulose and also the relation between the α-cellulose content of the resulting pulp and the viscosity. In all cooks, chips from one and the same log were used and the composition of the cooking acid was 5 grams of SO_2 and 0.9 grams of CaO per 100 ml. The temperature was raised uniformly from 20° to 135° C in 10 hours.

Table 1 shows that the yield of pulp increases by well over 5 per cent for the same viscosity if the final temperature is increased from 130° to 150° C. While the α-content decreases in cooking down to lower viscosities at 130° C, a higher final temperature would cause an increase. A considerable increase in the yield of α-cellulose is also to be noted due to the increased velocity of reaction at higher temperatures in the hydrolysis of the wood polyoses. The sugar content of the waste liquor also increases with an increased final temperature.

The maximum obtained when plotting the α-content as a

Table 2.

CaO g/100 ml		0.60		0.75		0.90		1.05	
Temperature		135°	145°	135°	145°	135°	145°	135°	145°
Viscosity m. P.									
600	α-content	90.0	89.8	90.2	89.8	90.2	89.7	90.1	90.2
	α-yield	41.0	42.3	40.9	41.1	40.0	40.7	38.4	40.5
500	α-content	90.5	90.2	90.3	90.0	90.4	89.9	90.4	90.3
	α-yield	40.5	41.2	40.4	40.9	39.9	40.3	38.0	40.2
400	α-content	90.8	90.3	90.4	89.9	90.2	90.0	90.0	90.3
	α-yield	39.9	—	39.7	40.2	37.4	39.6	36.0	39.7
300	α-content	90.8	90.3	90.7	89.9	—	90.2	89.4	90.6
	α-yield	38.6	40.8	38.8	39.6	—	38.8	32.2	39.3
200	α-content	90.4	90.1	90.1	90.1	—	90.0	—	90.8
	α-yield	36.6	39.3	36.8	38.5	—	38.2	—	38.6

function of the viscosity moves towards lower values of viscosity at higher temperatures.

The effect of the lime content during the later stages of the cook is illustrated by Table 2, which is an excerpt from the mass of experimental data. In this case also chips from one and the same log were used in all cooks. The SO_2 content of the acid was 5 grams and the lime content varied from 0.6 to 1.05 grams per 100 ml. In this table the α-content and the yield of α-cellulose have been arranged in relation to the lime content and the viscosity at the two final temperatures 135 and 145° C.

All of the cooking series showed that the yields of pulp and α-cellulose at a certain viscosity depended upon the lime content, that is, the yields decreased with an increased lime content. It thus appears to be of no essential consequence whether the velocity of reaction is increased by decreasing the lime content or by increasing the temperature. In either case the result will be an increased yield at one and the same viscosity. It was also confirmed that the sugar content of

the waste liquor was augmented by a decreasing content of lime.

These cooks were carried out without relieving the digester of gas. Separate experiments have shown, however, that identical conditions exist in regard to the effect of temperature and lime content when the cooks are relieved to a constant maximum pressure (5 atm.).

The tendency of the native lignin to condense during the sulphite cooking determines to what extent the velocity of reaction may be increased in the manner described above. In technical operation, therefore, the conditions of cooking must primarily be chosen so as to ensure a normal dissolution of the lignin. This requirement being satisfied, attention may be given to desired improvements of quality during the processing. A thorough penetration of the cooking acid into the wood is of paramount importance with respect to the dissolution of the lignin. In this connection it may be mentioned that The Svedberg and co-workers have shown that the impregnation also affects the polydispersity of the sulphite cellulose. Sedimentation measurements have thus shown the numerical value of $\frac{"dB"}{dx}$ to be for instance 0.58 for a pulp produced with a very long impregnating period, while the value was 0.75 when normal period was used for impregnation. In this connection it is of interest to note the statements of Schieber (70) and Dörr (71) according to which the polydispersity of rayon pulp is an important point in the production of high quality artificial silk and cell wool. Löbering (72) is of the opinion that a low polydispersity should be a prerequisite for rayon pulps.

Our knowledge concerning the change of the polydispersity for different conditions of cooking is still insufficient. This is also the case with respect to the shape of the molecules, a question of great importance for instance in regard to the properties governing the viscosity of solutions of cellulose. The investigations carried out so far in this field may only be considered as preliminary. It is, however, reasonable to hope for a full elucidation of this problem by the work in progress at the Institute of Physical Chemistry in Uppsala under the direction of Professor The Svedberg. Part of this

work is devoted to investigations concerning the polydispersity and structural changes of the cellulose molecule during the final stages of the sulphite cooking.

Conclusion.

The chemical reactions taking place when wood is digested with sulphite cooking acid may be considered as fairly well known, although exact knowledge is lacking concerning the details of the constitution of lignin, and the reactions between lignin and sulphite. The hemicellulose constituents of wood and their behaviour during the process have also been subject to many investigations. On the other hand the fate of the cellulose has been astonishingly little considered. We know very little about the reactions of cellulose during the process, the changes in its molecular shape and the polydispersity, and the possibilities of managing the process in order to obtain a cellulose product with properties best suited to different technical purposes. Extended studies to acquire better knowledge in these directions are important and necessary.

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On Wood Cellulose as a Raw Material in Chemical Industry.

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Since the year 1846 when Schönbein (1) first prepared cellulose nitrate, cellulose has been subjected to chemical processes of many different kinds. The cellulose thus transformed now plays an important rôle both in our daily lives and in many special uses. One need only call to mind artificial silk, staple fibre, transparent wrapping, film, guncotton, lacquer, and so on. Cellulose nitrate in the form of celluloid (Hyatt, 1869 (2)) was the first of a series of plastics which have today found versatile application in the manufacture of objects of widely different kinds, and cellulose still retains its place as the most important raw material for high-polymeric products. In connection with the researches carried out with the help of physico-chemical methods by The Svedberg and his collaborators concerning the structures of cellulose and cellulose derivatives, it may be of interest to consider briefly the employment of cellulose as a starting material in contemporary chemical industry and especially to treat in some detail the problem, most important for this country, as to how far cellulose prepared from wood can be used for this purpose. It must, however, be emphasised that the account is primarily based upon conditions in Europe. Owing to the limited communications with the West it has unfortunately not been possible to follow the development, certainly considerable, which has occurred in America in this sphere during the war.

To begin with a short review will be given of the most important cellulose derivatives and their uses. Cellulose which has been chemically more or less transformed occurs mostly

in three variations, namely dissolved and thereafter regenerated cellulose, cellulose esters and cellulose ethers.

In the viscose process cellulose is first converted by mercerisation into alkali cellulose, which after grinding and ripening is turned into xanthogenate by treatment with carbon bisulphide. Dissolving in weak caustic soda solution gives the so-called viscose. After filtration and ripening the viscose is pressed out through nozzles of desired form into a coagulation bath containing sulphuric acid and salts. After the product has undergone certain subsequent treatments, it is ready as regenerated cellulose in the form of rayon, staple fibre, cellophane, sponges, capsules etc. Quantitatively the viscose process is the most important chemical method for the working up of cellulose. Its development has gone forward with extraordinary rapidity. After Cross, Bevan and Beadle (3) first carried out the process on the laboratory scale in 1891, it was only a few years before the first artificial silk production by this method was commenced. In 1910, production was 8 000 tons; in 1920, 25 000 tons; in 1930, 200 000 tons. In 1929, the actual manufacture of staple fibre began. In 1939, 490 000 tons of rayon and 520 000 tons of staple fibre were produced. Now the total world production of viscose products amounts to about 1 200 000 tons a year.

In Sweden, artificial silk and staple fibre are produced according to the viscose method by *AB Svenskt Konstsilke*, Borås, staple fibre by *AB Cellull*, Älvenäs, and staple fibre, transparent wrapping and other products by *AB Nordisk Silkecellulosa* in Norrköping, the total output being about 17 000 tons per annum.

In the so-called copper-silk method, first reported by Despaissis (4) in 1890, cellulose is dissolved in ammoniacal copper hydroxide solution. It is reprecipitated in the form of threads by ejection through fine nozzles into water and simultaneously stretched. By this method silk and staple fibre of high quality are prepared, usually known as *Bemberg* products. Copper-silk is not produced in Sweden.

Vulcanized fibre may also be counted among the regenerated cellulose products. In its preparation cellulose is allowed to swell in zinc chloride solution, is pressed, rinsed with water

and dried, when a hard, homogeneous and resistant product is obtained. This is employed in the manufacture of trunks and suit-cases, certain machine components etc. Vulcanized fibre is produced in Sweden by *AB Tidan,* Mariestad.

The most important of the cellulose esters are the nitrate and the acetate. The nitrate has already been briefly mentioned. It is prepared by treatment of cellulose with a mixture of nitric and sulphuric acids with subsequent stabilisation and drying. Cellulose nitrate, in the form of guncotton, is the most important propellent for projectiles, and its production abroad for military purposes must now amount to several hundred thousand tons per annum. The civil consumption is also considerable. Cellulose nitrate sells at a relatively low price and has extraordinarily good properties. It is still unexcelled in its use as photographic film, but has a disadvantage in its great inflammability. Cellulose nitrate of several varieties, for lacquers etc., is produced in Sweden by *AB Bofors, Nobelkrut.* For military purposes it is also made elsewhere in the country.

Cellulose acetate is made by the acetylation of cellulose with acetic acid, acetic anhydride and a catalyst. The triacetate is thus obtained, and subsequent partial hydrolysis gives a lower degree of acetylation. The triacetate, also called the primary acetate, was first made by Schützenberger (5) in 1865. Only after the discovery by Miles (6), in 1903, of the partial hydrolysis, however, a practicable product was obtained. This offered, among other things, the advantage of being soluble in acetone, and cellulose acetate rapidly found important applications in the manufacture of artificial silk, transparent wrapping, non-inflammable film, lacquers, safety glass and plastics. An especially marked increase in the cellulose acetate production has taken place during the last twenty years. In the manufacture of acetate silk, which takes place to a quite important extent, an acetone solution of cellulose acetate is used which is pressed out through a nozzle with fine holes into a warm current of air, where the solvent evaporates and threads are formed. In recent years the primary acetate has also begun to find certain applications. Cellulose

acetate is not yet produced in Sweden, despite the fact that we possess all the necessary raw materials.

More recent than the cellulose derivatives described above are the cellulose ethers, which were first mentioned in the literature by SUIDA (7) in 1905, and whose preparation was first described in patents granted in 1912 to BAYER & Co. (8), LILIENFELD (9) and DREYFUS (10). During the last two decades, their large scale factory production has begun, especially in Germany and the U. S. A. The most important are methyl, ethyl and benzyl cellulose and ether-carboxylic acid salts such as sodium cellulose glycolate. Certain such products are soluble in water and are excellent materials for glues, pastes and geling agents. Others are soluble only in organic solvents and are used for lacquers, insulating materials, plastics etc. The manufacture of cellulose ether products has been taken up recently in Sweden by *Uddcholms Aktiebolag* and *Svenska Cellulosaaktiebolaget.*

In all the fields of chemical application enumerated above, cellulose was first used in the form of cotton or cotton linters, the latter material consisting of the short seed-hairs from the cotton plant, which are not sufficiently long to be used in spinning, but which have the same chemical composition as cotton. Thus after a relatively simple purification, consisting of cleaning, boiling with alkali and bleaching, they give an almost pure cellulose. Some typical analyses of linters are given in Table 1. These and all other analyses recorded below were carried out in the cellulose laboratory of the Skoghall works.

At a very early stage, however, it became clear that wood cellulose, which is considerably cheaper than linters, could be used as raw material in the viscose process. Bleached sulphite cellulose was used, and the most desired properties of this were a good alpha cellulose content and uniformity of viscosity and other characteristics. Bleached sulphite cellulose had previously been used only in the manufacture of paper, where such great demands upon its quality were not made. At the factories which made this first silk pulp, it was long feared to make any changes whatever either in the production method or the machinery, which was thought would affect the pro-

Table 1. Analyses of Cotton Linters.

	Crude linters		Bleached linters			
Alpha cellulose . . . . . % (after Cross & Bevan)	96.0	99.1	98.9	99.0	99.3	98.6
Pentosans . . . . . % (after Tollens-Kullgren-Tydén)	1.2	0.7	0.5	0.7	0.4	0.7
Resins and fats . . . . . % (Alcohol extract)	1.1	0.3	0.12	0.21	0.11	0.08
Ash . . . . . %	1.3	0.2	0.11	0.08	0.05	0.07
Viscosity . . . . . Cp (after Tappi, 1 % in cupra-ammonium. 20° C)	1 100	400	200	65	43	17

perties of the pulp and thus cause disturbances in the viscose factory. The production of both pulp and rayon thus were processes in which as late as twenty years ago the knowledge was mostly empirical, and consequently they were shrouded in considerable secrecy.

Gradually, however, there grew a more thorough knowledge of the viscose process and with it a greater aptitude on the part of the rayon manufacturers to try new methods and improved raw materials. The new cellulose qualities, which became available in the nineteen-thirties, gave a higher yield, a better quality of rayon, and certain working advantages in the viscose process. An essential factor in this improvement in the quality of the silk pulp, or, as it is now called, the viscose pulp, has been the introduction of better bleaching and boiling systems, which have brought about that in the most modern factories a viscose pulp can be prepared with almost any desired analytical data over a considerable range. By way of example, Table 2 shows typical analyses of viscose cellulose of older date and of the most recent type. The pulps mentioned in the table were prepared from Swedish spruce wood by the sulphite method. A very essential difference between the older and newer qualities, which does not appear in the table, lies in their whiteness. The modern viscose pulps, especially the so-called "super-qualities", which

Table 2. Analyses of Viscose Cellulose (Sulphite) from Spruce.

	Viscose pulp of year 1924	Viscose pulp of year 1944	
		"Normal quality"	"Super quality II"
Alpha cellulose . . . . . %	87.0	89.0	91.0
Pentosans . . . . . %	3.8	2.7	2.7
Alcohol extract . . . . . %	0.85	0.60	0.30
Ash . . . . . %	0.22	0.09	0.09
Viscosity . . . . . Cp	30	25	25

are mildly treated with alkali, are freed almost completely from residual lignin and thus have a high degree of whiteness, giving a silk which in most cases requires no bleaching.

Scandinavian spruce has from the beginning been considered the best raw material for viscose pulp, and is so still, even if certain American species, such as the Western Hemlock, which is now being exploited on a large scale, must be considered to stand quite on the same level. During the past decade a great effort has been made in certain countries, especially Germany, Italy, and Japan, to attain self-sufficiency also in respect of cellulose, and it has been attempted to manufacture viscose pulp on a large scale from domestic raw materials. In Germany beech-wood was the principal starting material, and it soon proved that from this a quite good cellulose could be prepared, even if it did not reach the standard of the Scandinavian pulps. A special disadvantage was the typical high pentosan content of deciduous wood. Viscose pulp from beech is now manufactured in Germany in very great quantities. In Italy, which is poor in forests, the rayon concern *Snia Viscosa* built a magnificent plant for the production of silk pulp from giant reed, *Arundo donax*, which was planted on formerly uncultivated marshland at the northern end of the Adriatic Sea. In order that this material, which contains, among other things, much silicic acid, may give a utilisable viscose pulp, the cellulose prepared therefrom by the sulphite process must be subjected to violent treatment with alkali etc., which also makes the process expensive. However, a quite practicable

viscose pulp with very good analytical figures has been obtained. In Japan an attempt has been made on similar lines to utilise the available raw materials, such as the Soya plant in Korea, and it appears that at present the great Japanese rayon and staple fibre industry is largely supplied with home raw materials, although the quality of these seems to leave much to be desired. Table 3 gives analyses of German beech cellulose and Italian *Arundo donax* pulp.

Table 3. Analyses of Viscose Cellulose from Deciduous Wood and Reeds.

	Beech	*Arundo donax*
Alpha cellulose . . . . . %	89.0	97.0
Pentosans . . . . . %	6.0	2.4
Alcohol extract . . . . . %	0.80	0.85
Ash . . . . . %	0.17	0.10
Viscosity . . . . . Cp	25	70

The analysis of a viscose cellulose, or of cellulose in general, leaves much unsaid about the properties of the pulp, however completely it be performed. Certain important properties do not appear, or appear only to a slight degree, in the analytical results. It is, for example, of the greatest practical importance that the viscose obtained can be filtered without the filter cloth becoming clogged up too rapidly. This presupposes that the cellulose can be mercerised and xanthogenated easily and evenly, which in turn depends to a great extent upon its colloidal state. In unfavourable cases the viscose will contain a large quantity of incompletely dissolved, gel-like fibre residues, which rapidly clog up the filter. This is the case, for example, with ordinary bleached sulphate cellulose, and has hitherto prevented its use in the usual viscose process. In recent years it has, however, been found possible in Germany to achieve a satisfactory filtration by means of a modification in the mercerisation process and direct transference of the pulp from the cellulose mill to the viscose factory without preliminary drying. Furthermore, according to Phrix, the in-

troduction of a so-called pre-hydrolysis of the wood with weak acid before the alkaline treatment will give a cellulose with good filtering properties. They have even succeeded in preparing an employable viscose cellulose from straw with the help of pre-hydrolysis. Table 4 shows typical analyses for two viscose pulps prepared from pine wood by the sulphate process.

Table 4. Analyses of Viscose Cellulose (Sulphate) from Pine.

	Normal	Pre-hydrolysed
Alpha cellulose . . . . . %	88.0	94.5
Pentosans . . . . . %	6.0	3.0
Alcohol extract . . . . . %	0.05	0.03
Ash . . . . . %	0.15	0.10
Viscosity . . . . . Cp	14	16

With regard to the strength properties of the final silk or staple fibre, by which are meant breaking length, elasticity, and wearing properties, no appreciable differences can usually be observed when celluloses of good, normal qualities are used as raw materials. The properties are largely dependent upon the mode of manufacture in the viscose factories. Nevertheless, in the case of the pre-hydrolysed sulphate pulp mentioned above a definite improvement in the strength properties can be observed in comparison with sulphite pulp. Investigations carried out up to the present indicate that this is associated with lower polydispersity of the sulphate cellulose, which is confirmed by the observations recorded by Gralén in his recently published doctoral thesis (11).

In other respects also a difference between celluloses prepared under acid and alkaline conditions can be demonstrated. Thus the ripening of alkali cellulose, measured by the fall in viscosity, takes place considerably more slowly for sulphate than for sulphite cellulose. Here we may recall the disagreement, found in Gralén's experiments, in the relationship between the viscosity in cuprammonium hydroxide and the sedimentation data. Differences can also be seen in the ripening

behaviour of the viscose. A large number of problems, partly of great immediate practical importance, here await their solution.

In no other chemical sphere has wood cellulose become so dominant as in the viscose process. Linters are now used there only to an extremely small extent and then only for quite special purposes. It is considered, however, that by the use of linters or by their admixture, improvements in certain properties may be imparted to the silk. That it is not only a matter of the purity of the raw material is shown by the fact that linters, in these special cases, cannot be replaced by the modern refined celluloses, despite the fact that the latter show practically the same analytical data. The reason obviously lies deeper.

Until a few years ago linters had been used almost without exception in the manufacture of copper-silk. Owing to import difficulties, however, certain countries have been obliged to start using wood cellulose; this has succeeded better than one dared to hope. For this purpose the minimum demands regarding the purity of the cellulose are higher than in the viscose process, and for higher qualities of silk so-called high alpha cellulose is employed. This signifies wood cellulose which has been subjected to certain after-treatment in connection with the bleaching process, usually with alkali, with the idea of removing impurities such as resin, pentosans and low-polymeric hexosans, and simultaneously increasing the alpha cellulose content. Analyses on a number of samples of high alpha cellulose, some of Swedish and some of foreign origin, is given in Table 5 on page 410. If a comparison is made between the analysis of pulp No. 2 in Table 5, which is a Swedish high alpha sulphite cellulose from spruce, with that of linters in Table 1, the difference is found to be very small. When used in the copper-silk process, however, they behave rather differently, and certain changes in the spinning process and, for example, the conditions of drying, must be made when wood cellulose is employed. Nor can a mixture of linters and wood cellulose be used. When the process is suitably adapted, however, the use of high alpha cellulose of a suitable type gives a result practically as good as that of linters.

Different types of cellulose nitrate are prepared which principally differ in their nitrogen contents. The lowest degrees of nitration, corresponding to about 11 per cent N, are used for celluloid, the intermediate degrees (11.5—12.5 per cent N) for lacquers, photographic films etc., and the highly nitrated products (about 13 per cent N) for guncotton. For all these purposes the starting materials were formerly cotton and linters exclusively. An exception must be made for a period during the last World War, when certain countries were compelled to employ ordinary bleached sulphite pulp to cover their tremendous consumption of cellulose for the manufacture of guncotton. This raw material left much to be desired. Thus the alpha cellulose content appears to have been only about 80—85 per cent, the resin content was about 1 per cent and the ash about 0.5 per cent. The consequence was that the guncotton had low stability, and could not be employed except under war conditions when it was rapidly used up. After the war the use of linters was resumed. In the beginning of the last decade, circumstances were completely changed by the introduction of the modern bleaching and refining methods for wood cellulose. The first completely satisfactory cellulose for nitration appears to have been one prepared about ten years ago in Sweden, namely the one given as No. 5 in Table 5. It was a highly purified sulphate cellulose, which gave such good results that it was even considered to be in som respects superior to linters. In the period that has since elapsed, success has also been attained in the preparation of purified sulphite pulps suitable for nitration. These can also be used with excellent results as substitutes for linters in cellulose nitrate for lacquer, celluloid etc. It is mostly high alpha cellulose of type 2 in Table 5 that is employed. When used for these purposes unrefined celluloses give definitely unsatisfactory results with regard to whiteness, clarity and stability of the final products.

At present high alpha celluloses prepared by both the sulphite and sulphate methods are used for purposes of nitration. Unrefined sulphite pulp appears also to be used abroad for guncotton manufacture. It is important, however, in nitration, just as in acetylation, where the cellulose is treated in

Table 5. Examples of Some European High Alpha Celluloses.

No.	1.	2.	3.	4.	5.	6.	7.
Raw material	spruce	spruce	spruce	pine	pine	beech	beech
Method of preparation	Sulphite	Sulphite	Sulphite	Sulphate	Sulphate	HNO_3	Sulphite
Alpha cellulose . . %	94.5	98.0	98.4	94.0	96.0	97.7	94.5
Pentosans . . . . . %	2.5	0.8	0.8	2.4	2.4	1.6	2.3
Alcohol extract . . %	0.08	0.09	0.08	0.04	0.05	0.15	0.17
Ash . . . . . %	0.07	0.04	0.06	0.08	0.08	0.11	0.15
Viscosity . . . . . Cp	40	40	100	15	35	20	32

acid solution and consequently does not swell so much in the reaction mixture, that a rapid and complete permeation with acid be attained. The absorbency of the cellulose fibres is therefore of great importance. Furthermore, the pulp should not be introduced into the process in the form of hard sheets, but rather defibrated or converted into crêpe paper.

An advantage over linters enjoyed by cellulose of high quality which becomes obvious in its use for nitration purposes is its considerably greater uniformity. For instance, in a good cellulose for chemical use the viscosity is constant within the limits ± 10 per cent.

Especially great demands are made on cellulose which is to be used as raw material in the manufacture of cellulose acetate. It must be able to absorb the acetylation liquid quickly and evenly, which imposes special conditions regarding its physical form. Non-acetylatable components may only be present in insignificant amounts, which necessitates that the cellulose be freed very thoroughly from impurities. Finally the acetylation and hydrolysis reactions must proceed evenly; the cellulose must therefore be so homogeneous in chemical respect that certain carbohydrate chains do not react considerably more quickly or slowly than the majority. If the above conditions are not satisfied, an inferior acetate is obtained, which, among other things, contains incompletely acetylated fibres and gives turbid solutions. In the preparation

of transparent objects, films etc. it is an absolute condition that the acetate shall give clear solutions in acetone, while for silk the demands on clarity are not so great. For acetylation linters were formerly used practically exclusively. As a consequence of the blockade, however, certain countries have been obliged in recent years to go over to high alpha cellulose. The experiments have been successful. The preparation of the cellulose in the form of crêpe paper or some similar form and the introduction of a suitable pre-treatment at the acetate factories has contributed to the success in achieving the necessary uniformity of acetylation. As certain cellulose manufacturers have been able to supply a cellulose which is suitable as a raw material in respect of both chemical purity and mild mode of preparation, a relatively good result has been achieved. In the making of the highest qualitities of acetate the difficulties, however, have been very great. Nevertheless it may be said with confidence that even the most exacting consumers can now have their requirements filled. In the most demanding cases use has been made, for example, of high alpha celluloses of types 2 and 4 in Table 5, whereas in those cases where it has been possible to employ somewhat lower qualities, pulps of types 1 and 7 have been taken. That analytical data are not in themselves decisive follows from the fact that cellulose of type 7 has sometimes given almost as good results as type 2, while the sulphate celluloses 4 and 5 have proved quite unsuitable. With regard to strength and elasticity of the final products, the difference between acetates from high alpha cellulose and acetates from linters seems to be very small.

The preparation of cellulose ethers puts equally great demands on the raw material. In the preparation of these, which was started during the last few years at the Skoghall works, we have made very interesting observations concerning the important rôle played by the quality of the cellulose. Thus essentially different results are obtained with cellulose prepared by the sulphite and sulphate methods. The results indicate that cellulose ethers of the highest quality can be prepared from wood cellulose. The development in these branches of manufacture will therefore receive great assistance from the

rich experience in the field of cellulose production which has been accumulated in this country.

With the above account it has been the intention to show the practical economic background of present-day cellulose research and at the same time to draw attention to some of the many still unsolved chemical and physico-chemical problems to be encountered in the chemical treatment of cellulose. We have reason to hope for a continued favourable development of the Swedish chemical industry based on the applications of cellulose. A more thorough knowledge of cellulose and the structure of its compounds is of the greatest value in the development of this industry. It is therefore with the profoundest satisfaction that we welcome the scientific researches which of late years have been increasingly pursued in this sphere.

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An Example of the Use of Adsorption Analysis in Technical Synthesis.

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It might almost be said that organic synthesis is now passing through its hydrocarbon epoch. Hydrocarbons are cracked, hydrogenated, alkylated and polymerised. Around the oil refineries a chemical industry is growing, where all imaginable organic-chemical products are manufactured, from solvents to artificial resins and synthetic rubber. Those countries which have no natural gas at their disposal prepare their hydrocarbons from alcohol or carbon and water.

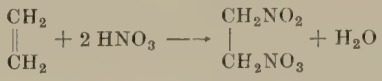
Many industries which cannot employ hydrocarbons as raw materials for their processes have, nevertheless, had completely new semi-manufactured products placed at their disposal by the said development. In the manufacture of explosives, for example, glycerine has largely given place to glycol.

It is naturally the endeavour of the technologist to avoid as far as possible all intermediate processes and to make his products direct from the raw materials. The development of such direct syntheses has been considerable in recent years. A characteristic feature of such direct syntheses is, however, that they do not give rise to one, but to a number of different compounds. The analysis of such mixtures has often proved to constitute a really difficult problem.

For the last ten years great attention has been devoted at the laboratory of the *Nitroglycerin AB* to the problem of preparing explosives direct from unsaturated hydrocarbons. The analytical problems here arising have been partially solved by the use of the adsorption method worked out by Tiselius (1, 5, 6) and Claesson (4, 5). These researches give a good illustra-

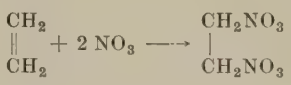
tion of this method's applicability in modern technical organic synthesis. A short description would therefore appear well motivated.

The direct nitration of olefines with nitric acid gives, besides nitric acid esters, substances which are both nitro compounds and nitric acid esters (7—9).

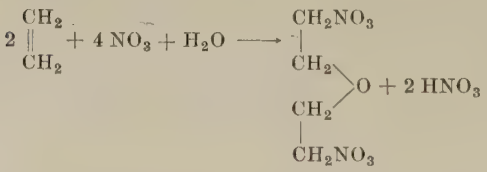


These compounds are very unstable products and are not suitable for use as explosives. Investigations att *Gyttorp* have shown, however, that if the nitration is carried out in a strongly oxidising environment, the formation of nitro compounds can be completely suppressed in favour of nitric acid esters. A simple manner of performing this nitration has been shown to be electrochemical nitration at an anode, which gives a high overpotential (10—12). The products formed during the electrolysis have been given the common name of "oxinites". The main reactions in this process have proved to be of the following types:

1.



2.



It may be discussed whether the anode film in its reaction with ethylene has a potential energy corresponding to free NO_3 radicles or whether the somewhat lower energy stage $HNO_3 + O$ is associated with the main course of the esterification. Fichter (13, 14) and collaborators, who have performed interesting electrochemical experiments with mixtures of propionates and nitrates and have identified nitroglycol and other nitric acid esters among the products, deny that esterification occurs by the direct addition of NO_3 radicles. The present

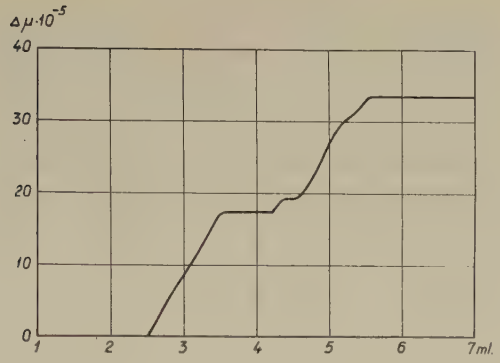


Fig. 1. Front analysis of ethylene-oxinite.

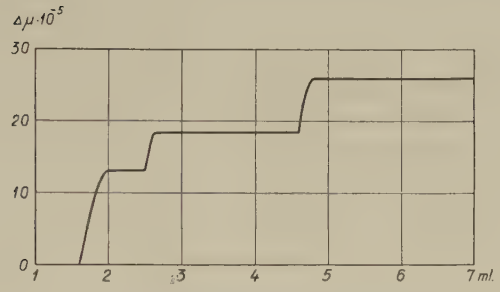


Fig. 2. Front analysis of ethylene-oxinite to which an equal quantity of n-butyl nitrate had been added.

author cannot share FICHTER's opinion in this matter. It is, indeed, probable that both types of reaction take place, and that the partition between them is determined by the current density, the water content and other physical and chemical factors.

Since it is probable that in propionate electrolysis the nitric acid esters are formed from the ethylene split off in the electrolytic process, this esterification in statu nascendi is not fully comparable with the electrolysis of nitrates under the introduction of ethylene.'

In his product FICHTER does not find diglycol dinitrate but butanediol dinitrate. He also finds ethyl nitrate and n-butyl nitrate. In samples from the *Gyttorp* process hitherto analysed, which admittedly were prepared only at high current density, we have been unable to detect butanediol dinitrate. Lower current density might concievably give rise to this compound.

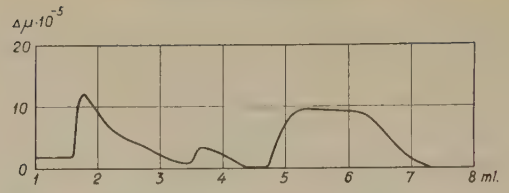


Fig. 3. Development analysis of ethylene oxinite.

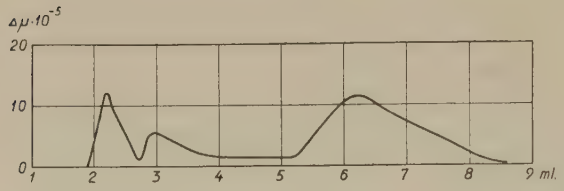


Fig. 4. Model experiment with a mixture of pure nitro-glycol, butyl nitrate and diglycol dinitrate.

On the other hand n-butyl nitrate and ethyl nitrate have been found in small quantities.

The most complete adsorption analysis so far has been performed on an ethylene oxinite produced under the same conditions as would prevail in large-scale manufacture.

Before the adsorption analysis the product was subjected to a vacuum distillation in which 10 per cent was distilled off. The adsorption analysis was then carried out both on mobile distillate and on the ethylene oxinite residue.

Fig. 1 shows the front analysis of the residue and Fig. 2 that of the same product to which an equal quantity of n-butyl nitrate had been added. A comparison of the two diagrams shows that the second "step" corresponds to n-butyl nitrate. In the same manner it was established that the first "step" corresponded to nitroglycol and the third to diglycol dinitrate.

Fig. 3 shows a development analysis of the ethylene oxinite and Fig. 4 a model experiment with a mixture of pure nitroglycol, butyl nitrate and diglycol dinitrate. By integration of the curves and "setting" against the model experiment the quantitative composition could be calculated:

Butyl nitrate	4.4 per cent
Diglycol dinitrate	60.8 » »
Nitroglycol	34.8 » »

Nitrogen content found in nitrometer . . . . 15.64 per cent
» » calculated for a mixture of
above composition . . . . . 15.62 » »

It was found in the same way that the volatile fraction contained nitroglycol, butyl nitrate and some ethyl nitrate. According to an approximate calculation the original oxinite had the following composition:

Ethyl nitrate	1	per cent
Butyl nitrate	5	» »
Diglycol dinitrate	56	» »
Nitroglycol	38	» »

The investigations will continue in order to study in more detail the composition of the oxinites as a function of current density, flow velocity and other factors. The experiments so far performed have shown that adsorption analysis is capable of solving, in a quite elegant fashion, many analytical problems in technical syntheses of the type described.

The author wishes to express his respectful thanks to Professor The Svedberg, who has been kind enough to place the technical and scientific resources of the Institute of Physical Chemistry, University of Uppsala at our disposal, and to Professor Arne Tiselius and Fil. lic. Stig Claesson for much good advice in the course of this research.

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A Dielectric Investigation of Serum Proteins Treated with Alcohol and Ether.

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In a previous work (1) it has been shown, that the dipole moment and the time of relaxation of serum albumin and serum γ-pseudoglobulin are practically constant. The dielectric constants for a total serum are, at all wave-lengths, the sums of the corresponding values for the separated albumin and globulins multiplied by their percentage concentrations. In other words, the shape and internal electrical structure are not changed at the separation, and it is unimportant whether the separation be done by electrophoresis or by precipitation with saturated ammonium sulphate. The first method is unsuitable for the preparation of albumin, as the samples obtained are not stable, their conductivity increases rapidly, and they are totally spoiled (flocculated) in a week at $+4^\circ$. This disagreeable property is probably due to the proteolytic enzymes, which move together with the albumin in the electrophoresis. However, this effect can be eliminated by adding to the solutions a poison acting on proteolytic enzymes (2), $KBrO_3$, 2 mg for each gram protein.

Dielectrical measurements can only be investigated with any accuracy in samples with a conductivity of less than $10^{-4}\ \Omega^{-1}$ cm. The greater part of the ions must be eliminated by simple dialysis or by electrodialysis. Samples prepared in these different ways have the same properties, but electrodialysis is preferable, as it saves time and can be performed with greater accuracy. In any case some of the globulins, the euglobulins, will precipitate, and their dielectric properties remain impossible to measure. The main part of the globulin, the γ-pseu-

doglobulin, has a dipole moment of about 52 debyes, or approximately as much as a chain molecule of the same magnitude. According to this result obtained in my previous work, γ-pseudoglobulin must be considered an unstable molecule, without any quadripolar bonds. The albumin has a dipole moment of normal magnitude 18 debyes, and is also rather stable. The dielectrical properties of α- und β-globulins have not hitherto been examined, owing to lack of material.

In electrophoresis of lipid-free serum, Blix (3) found that α-globulin is the only one which is changed by extraction of lipids. It is remarkable that this stability is also valid for the β-globulin, though its content of lipids, calculated from the high specific volume, as found by Pedersen (4) for human sera, is about 50 per cent. The question is now whether the internal structure of the albumin and γ-globulin is changed or destroyed when the lipids, forming one twelfth of the total dry protein bulk, are removed. The usual method of doing this, the "wet way", consists in pouring out the serum solution into a large quantity of absolute alcohol just below 0°. The precipitate is then washed with alcohol and ether. The method is effective but violent; when carried out at a higher temperature, the precipitate will remain insoluble. In this investigation a gentler but less effective method was used. The serum preparations were frozen to $-18°$ and dried in vacuo. The serum powder obtained was placed in a Soxhlet-capsule, which was allowed to stand for a day in absolute (99.5 per cent) alcohol at $+4°$. The capsule with its alcoholic content was then extracted with ether in the Soxhlet-apparatus in the normal manner. The dry light-yellow powder is slightly soluble in water, and the velocity of dissolution increases with the serum content of the solvent. Clear solutions with a protein content of 10 per cent have been made.

During electrodialysis of these solutions no noteworthy precipitation takes place before the conductivity descends to about $5 \cdot 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. During the final electrodialysis, the greater part of the protein precipitates, so that the preparation obtained has a protein content of less than 1 per cent. Stronger solutions can be produced by evaporation, a process which is also ultimately associated with precipitation. Indeed, the low

concentration of these lipid-free serum proteins, combined with the small dielectric increment (small or normal dipole moments) and the inhomogeneity, make these substances rather unsuitable for dielectric investigations.

It is therefore all the more astonishing that the dielectric constants obtained fit the theoretical curve as well as can be seen from the figure.

Description of the samples:

Sample 1. Cow serum no. 15 frozen, dried and extracted, electrodialysed to $\varkappa = 0.84 \cdot 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. pH = 5.3. P-content 0.0093 mg/cc. (1.88 weight per cent P-lipid in the dry protein (4)). $c = 1.39$ weight per cent. $d_{25} = 1.0015$. s(albumin) = 4.51 S., s(globulin) = 6.33 S. 73 per cent albumin, 27 per cent globulin, no α- or β-globulin.

Sample 2. γ-pseudoglobulin from cow serum no. 16 precipitated and washed at pH 6.8 by 1/3 saturation with $(NH_4)_2SO_4$, preliminary dialysis against distilled water, frozen, dried and extracted with alcohol and ether, and dissolved in distilled water. Electrodialysis to $\varkappa = 1.65 \cdot 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. pH = 6.1. P-content = 0.0008 mg/cc. (0.2 weight per cent P-lipoid in the dry protein). $c = 1.10$ weight per cent. $d_{25} = 0.99982$. $s = 4.49$ S., heavier particles in the solution to about 20 per cent. (Confirmed electrophoretically).

Sample 3. Albumin from cow serum no. 16. The globulins precipitated at pH 6.8 by 2/3 saturation with $(NH_4)_2SO_4$, preliminary dialysis against distilled water, frozen, dried and extracted with alcohol and ether, and dissolved in distilled water. Electrodialysis to $\varkappa = 5.45 \cdot 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (conductivity increasing rapidly with time). pH = 5.1. $c = 0.64$ weight per cent. For other data see sample 4.

Sample 4. Sample 3 concentrated to $c = 1.48$ weight per cent. $d_{25} = 1.0010$. pH = 5.1. P-content = 0.0085 mg/cc (1.6 weight per cent P-lipoid in the dry protein). $s = 4.73$ S., heavier particles less than 16 per cent. $\varkappa = 4.07 \cdot 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (conductivity rapidly increasing with time).

Sample 5. Albumin from cow serum no. 18 frozen, dried and extracted with alcohol and ether, dissolved in distilled water. The globulins precipitated from the solution at pH 6.8 by 2/3 saturation with $(NH_4)_2SO_4$. Dialysis and concentration by ultrafiltration and electrodialysis to $\varkappa = 0.91 \cdot 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. pH = 5.3. P-content 0.0083 mg/cc (1.8 weight per cent P-lipoid in the dry protein). $c = 1.30$ weight per cent. $d_{25} = 1.00029$. $s = 4.46$ S. Practically homogeneous.

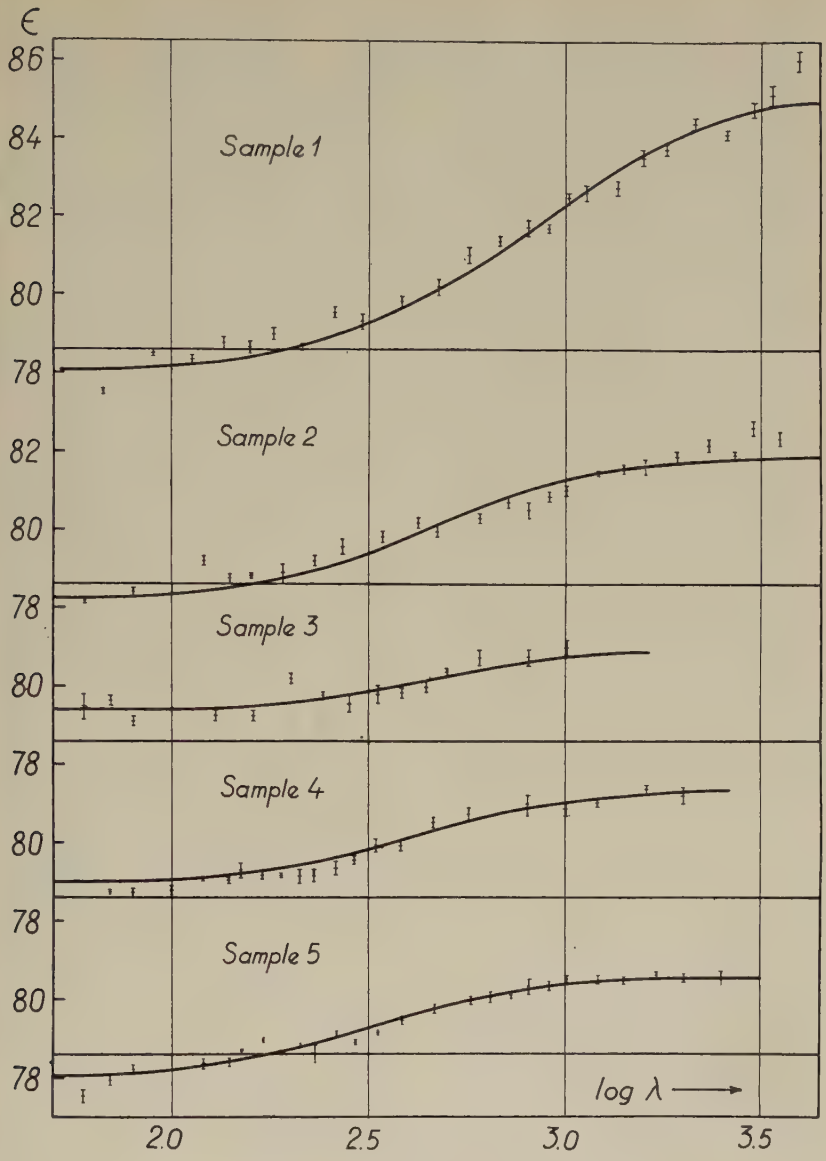
The measurements were made with a high-frequency bridge (6) working from 50 m to 6000 m. A variable cell of the "stamp" type was used. All parts of this capacity cell in contact with the solutions were made of pure silver. In the course of the measurements, the cell was reconstructed, so that the bearing for the stamp spindle is now also made of pure silver. The dipole moments were calculated in the usual manner, using the DEBYE formula. All measurements were made at $25.00° \pm 0.20°$.

Results.

The results for the total serum, Sample 1, seem to support the common opinion that the extraction does not change the structure of the albumin or the γ-pseudoglobulin. The values for albumin are taken from earlier experiments (1), and only one time of relaxation can be calculated from the data. Under these circumstances, the value $4.51 \cdot 10^{-7}$ sec. for the time of relaxation of the γ-pseudoglobulin must be said to agree favourably with the values formerly found. The dipole moment 61.0 D., likewise, cannot be said to be remarkably higher than the mean value of the former results, 53 D.

The dipole moment 17.5 D. of the pure albumin, sample 5, is exactly identical with that of unextracted albumin. All the more astonishing is the time of relaxation, $1.65 \cdot 10^{-7}$ sec., which can only be explained by assuming a rotation of the albumin molecule around its short axis. The molecule, approximately considered as a rotational ellipsoid, has an axial ratio $b/a = 0.29$. As the time of relaxation for untreated albumin indicates a rotation mainly around the long axis of the molecule, the extraction must be said to change the internal structure of the albumin molecule.

The sedimentation constant 4.49 S. for γ-pseudoglobulin, sample 2, shows that this protein is split into halves by the extraction of lipoids. The time of relaxation of $2.32 \cdot 10^{-7}$ sec. agrees well with that of the half-molecules. These would rotate around their short axis, and have an axial ratio $b/a = 0.23$. The dipole moment 22.1 D. is rather low. The moment expected would be 37 D.



The results differing most from those of previous work on untreated sera derive from samples 3 and 4, where the separation of albumin is effected before the extraction. As all separations in this work were associated with the addition of

saturated $(NH_4)_2SO_4$, the precaution of adding $KBrO_3$ to the sample was not taken. This omission is the explanation of the different behaviour of these samples from that of sample 5. The high values of the time of relaxtion, viz. $2.53 \cdot 10^{-7}$ sec. for sample 3 and $2.12 \cdot 10^{-7}$ sec. for sample 4, may be attributed to the great errors which are unavoidable in work with such low protein concentrations. The dipole moments of 20.2 and 15.7 D. respectively also agree with the moment for untreated albumin and that found for sample 5. The difference, however, between these samples and the others lies in the lower asymptote of the dispersion curve ε_u. Generally, as can be seen in the figure, the dispersion curve crosses the line marking the dielectric constant of the solvent, in these cases water, at 25° $\varepsilon_w = 78.60$. At high frequencies (short wavelengths), the dielectric constants of protein solutions are lower than ε_w, and the decrement $(\varepsilon_w - \varepsilon_u)/c \cdot d$, where c is the concentration and d the density of the solution, is found to be 0.435 for practically all proteins. For samples 3 and 4, however, ε_u is greater than ε_w. One explanation of this discrepancy may be that the solutions contain smaller molecules than the

Table with Summary of Results.

	Albumin		γ-pseudoglobulin	
	Time of relaxation (sec. · 10^7)	Dipole moment (debyes)	Time of relaxation (sec. · 10^7)	Dipole moment (debyes)
Untreated material = former results	1.0	18	1.8 5.4	53
Sample 1 (unseparated serum)	1.7	17.4	4.51	61.0
Sample 2 (globulin)	—	—	2.32	22.1
Sample 3 (albumin)	2.53	20.2	—	—
Sample 4 (sample 3 conc.)	2.12	15.7	—	—
Sample 5 (albumin)	1.65	17.5	—	—

Sample 1.

Wave-length (metres)	Dielectric Constants		
	found	error	calculated
∞	—	—	85.30
3 500	85.50	0.25	84.93
3 000	85.13	0.27	84.82
2 700	84.74	0.19	84.71
2 300	84.13	0.12	84.52
1 900	84.41	0.16	84.22
1 600	83.77	0.13	83.89
1 400	83.53	0.20	83.58
1 200	82.72	0.18	83.24
1 000	82.61	0.20	82.66
900	82.51	0.11	82.34
800	81.69	0.09	81.97
710	81.72	0.20	81.61
600	81.38	0.09	81.10
500	81.02	0.19	80.59
420	80.18	0.22	80.14
340	79.78	0.15	79.67
270	79.29	0.19	79.22
230	79.56	0.14	78.96
190	78.66	0.07	78.71
160	79.01	0.16	78.53
140	78.64	0.15	78.43
120	78.81	0.14	78.33
100	78.35	0.09	78.23
80	78.50	0.05	78.15
60	77.52	0.05	78.08
0	—	—	78.00

"Effect" $= \varepsilon_s - \varepsilon_u = 7.30$

Standard deviation = 0.32

Sample 2.

Wave-length (metres)	Dielectric Constants		
	found	error	calculated
∞	—	—	81.90
3 500	82.34	0.21	81.84
3 000	82.59	0.18	81.82
2 700	81.91	0.10	81.80
2 300	82.15	0.14	81.76
1 900	81.35	0.16	81.70
1 600	81.61	0.18	81.60
1 400	81.50	0.16	81.54
1 200	81.38	0.11	81.43
1 000	80.97	0.10	81.26
900	80.86	0.14	81.14
800	80.47	0.17	80.99
710	80.68	0.15	80.81
600	80.29	0.11	80.54
500	79.94	0.15	80.21
420	80.16	0.13	79.89
340	79.79	0.15	79.52
270	79.55	0.21	79.16
230	79.20	0.12	78.95
190	78.85	0.25	78.74
160	78.81	0.04	78.60
140	78.75	0.11	78.52
120	79.20	0.13	78.44
100	78.47	0.13	78.37
80	78.37	0.12	78.31
60	78.17	0.08	78.26
0	—	—	78.20

"Effect" $= \varepsilon_s - \varepsilon_u = 3.70$

Standard deviation = 0.25

Sample 3.

Wave-length (metres)	Dielectric Constants		
	found	error	calculated
∞	—	—	81.10
1 000	81.01	0.20	80.77
800	80.73	0.22	80.68
600	80.73	0.19	80.41
500	80.34	0.11	80.25
440	79.98	0.13	80.14
380	79.82	0.12	80.01
330	79.81	0.19	79.90
280	79.52	0.20	79.79
240	79.76	0.11	79.69
200	80.20	0.14	79.60
160	79.23	0.13	79.52
130	79.24	0.14	79.48
100	79.42	0.06	79.42
80	79.11	0.13	79.40
70	79.62	0.12	79.39
60	79.48	0.34	79.38
0	—	—	79.35

"Effect" $= \varepsilon_s - \varepsilon_u = 1.85$

Standard deviation = 0.25

Sample 4.

Wave-length (metres)	Dielectric Constants		
	found	error	calculated
∞	—	—	81.40
2 000	81.22	0.21	81.30
1 600	81.33	0.15	81.25
1 200	81.06	0.11	81.14
1 000	80.86	0.17	81.04
800	80.94	0.28	80.89
570	80.73	0.17	80.56
460	80.52	0.13	80.31
380	79.94	0.16	80.08
330	79.92	0.18	79.91
290	79.57	0.10	79.76
260	79.35	0.17	79.65
230	79.15	0.16	79.53
210	79.14	0.15	79.46
190	79.17	0.07	79.38
170	79.17	0.11	79.31
150	79.31	0.21	79.24
140	79.08	0.08	79.20
120	79.04	0.02	79.14
100	78.81	0.13	79.09
80	78.72	0.12	79.04
70	78.74	0.04	79.02
60	78.11	0.19	79.00
0	—	—	78.95

"Effect" $= \varepsilon_s - \varepsilon_u = 2.45$

Standard deviation = 0.20

albumin, to an amount of 37 per cent of the protein in sample 3 and 29 per cent in sample 4. Another explanation would be that the smaller dipoles rotating in the high-frequency field were still chemically bound to the albumin molecule, in the same way as the ligands are bound in a chain molecule. The

Sample 5.

Wave-length (metres)	Dielectric Constants			Wave-length (metres)	Dielectric Constants		
	found	error	calculated		found	error	calculated
∞	—	—	80.60	290	78.89	0.06	79.17
2 500	80.53	0.20	80.56	260	79.10	0.08	79.03
2 000	80.55	0.07	80.53	230	78.60	0.22	78.88
1 700	80.65	0.04	80.51	210	78.79	0.04	78.78
1 400	80.45	0.08	80.47	190	78.64	0.05	78.67
1 200	80.49	0.11	80.43	170	78.94	0.04	78.57
1 000	80.45	0.12	80.36	150	78.66	0.05	78.47
900	80.35	0.11	80.31	140	78.37	0.11	78.42
800	80.32	0.20	80.24	120	78.35	0.12	78.32
720	80.09	0.08	80.17	100	78.47	0.12	78.23
640	80.06	0.10	80.08	80	78.20	0.12	78.15
570	79.96	0.09	79.97	70	77.92	0.11	78.12
460	79.74	0.11	79.75	60	77.54	0.13	78.09
380	79.45	0.10	79.52	0	—	—	78.00
330	79.14	0.04	79.34				

"Effect" $= \varepsilon_s - \varepsilon_u = 2.60$

Standard deviation = 0.14

latter explanation seems preferable, since the samples have undergone many and lengthy dialyses. Smaller molecules or chain molecules, however, are both created from the original albumin molecules by the action of the proteolytic enzymes, and the increasing conductivities of these samples are also due to their action. We can only conclude that the proteolytic enzymes are not destroyed by the extraction, and that the lipid-free albumin is more easily destroyed than the unextracted.

Summary.

1. Serum proteins extracted with alcohol and ether in a state of dryness have been dielectrically investigated.
2. The dielectrical behaviour of the extracted proteins differs

from that of the native proteins. The internal structure of the serum proteins is changed.

3. Only the more stable protein molecules have been investigated. The bulk of the extracted serum proteins precipitate during the dialysis.
4. Extracted serum albumin is more sensitive to proteolytic enzymes than untreated albumin.

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L'hémocyanine de *Helix pomatia* est-elle composée de deux espèces de molécules?

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Svedberg et ses collaborateurs (1, 2, 3) ont montré par des sédimentations dans l'ultracentrifuge que les hémocyanines sont des molécules géantes de poids moléculaire dans les limites de 500 000 environ jusqu'à 10 millions. Ils ont d'ailleurs trouvé que les hémocyanines sont dissociées en multiples bien définis par un changement du pH, cette réaction étant souvent réversible.

L'hémocyanine de *Helix pomatia* est dissociée en demi-molécules non seulement par une variation dans le pH mais aussi par l'addition d'un électrolyte ou non-électrolyte (4). Les constantes moléculaires de cette hémocyanine et de ses fragments de dissociation sont données dans le tableau 1. (Voir aussi 4.)

Tableau 1. Les constantes moléculaires de l'hémocyanine de *Helix pomatia* et de ses fragments de dissociation.

Composant	$(s_{20})_0$	D_{20}	M	L
Molécule entière	103,0	1,07	$8{,}91 \cdot 10^6$	890
Demi-molécule	65,7	1,41	$4{,}31 \cdot 10^6$	890
Huitième	19,7	1,77	$1{,}03 \cdot 10^6$	960

$(s_{20})_0$, la constante de sédimentation dans l'eau à 20° C et à la concentration zéro, est exprimé en Svedbergs et D_{20}, la constante de diffusion à 20° C, en unités de 10^{-7}. La longueur de la molécule L (donnée en Å) est déterminée au moyen de la biréfringence dynamique (5). Le volume spécifique partiel de la substance dissoute, V, est égal à 0,738.

Si l'hémocyanine de *Helix pomatia* est dissociée par l'addition d'un électrolyte, par exemple le chlorure de sodium, la dissociation augmente progressivement avec la concentration de l'électrolyte pour cesser subitement quand les trois quarts de l'hémocyanine sont dissociés (4). En augmentant la concentration de l'électrolyte, l'état de dissociation ne subit aucun changement. L'hémocyanine de *Helix pomatia* se comporte ainsi comme si elle était composée de deux espèces d'hémocyanines, l'une (A), dont la concentration est de 75 p. c., subissant dissociation par les électrolytes, l'autre (B) étant stabile aux électrolytes. Toutes les deux sont dissociées par le changement du pH. L'existence probable de ces différentes hémocyanines a été prouvée par les expériences suivantes.

Essai de séparation.

Nous avons effectué une séparation dans la centrifuge préparative de Beams (6) en utilisant une solution 1,0 M en NaCl et 0,08 M en tampon d'acétates, où la dissociation avait atteint sa valeur maxima c. a. d. 75 p. c. (Fig. 1 *a*, Fig. 2 B). La solution (*a*) est centrifugée jusqu'à ce que l'hémocyanine non dissociée se soit déposée au fond du tube. La solution séparée de son dépôt (*b*) est maintenant analysée à l'ultracentrifuge et

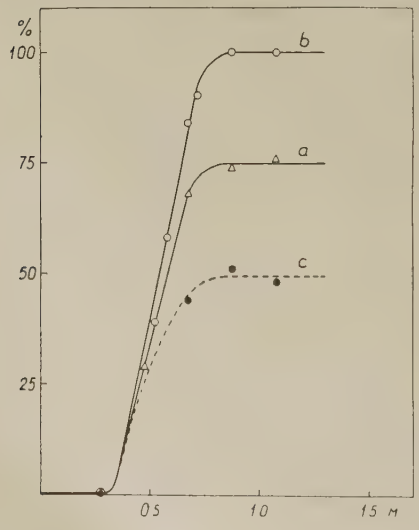

Fig. 1. Dissociation en demi-molécules en fonction de la molarité, M, des électrolytes.

a: L'hémocyanine originale.
b: L'hémocyanine, espèce A, complètement dissociée en demi-molécules quand la concentration des électrolytes est plus grande que 0,8 M.
c: La solution du sédiment d'hémocyanine contenant les deux espèces A et B dans des proportions à peu près égales.

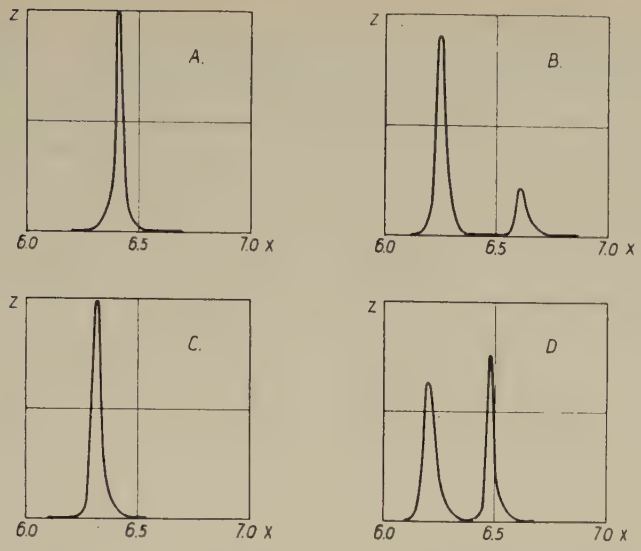

Fig. 2. Diagrammes de sédimentation montrant la séparation des deux espèces d'hémocyanines.

A: L'hémocyanine originale non dissociée (molécule entière). Solvant: 0,20 M-NaCl et 0,08 M tampon d'acétates. pH = 5,3.

B: L'hémocyanine originale dissociée maximalement par les électrolytes. Solvant: 1,00 M-NaCl et 0,08 M tampon d'acétates. pH = 5,2.

C: L'hémocyanine séparée, solution *b*. Même solvant que B. La solution ne contient que des demi-molécules.

D: Solution (*c*) dans laquelle le sédiment d'hémocyanine a été dissous. Même solvant que B.
Concentration de l'hémocyanine environ 0,3 p. c.

Force centrifuge 120 000 fois la force de la pesanteur; temps après avoir atteint pleine vitesse: 30 min. pour A, 40 min. pour B, 50 min. pour C et 35 min. pour D.

nous avons trouvé qu'elle ne contient que des demi-molécules (Fig. 2 C). Le sédiment de protéine est dissous dans la solution-tampon utilisée; le procédé de centrifugation et de dissolution est répété encore une fois. L'analyse par l'ultracentrifuge montre que la solution ainsi obtenue (*c*) contient plus d'hémocyanine non-dissociée (Fig. 2 D) que la solution originale (Fig. 2 B). Les solutions *b* et *c* sont stables: après un mois, la solution *b* ne contient toujours que des demi-molécules et la solution *c* montre la même relation de composition qu'auparavant entre hémocyanine dissociée et non dissociée. Si les deux solutions d'hémocyanines sont dialysées contre une solution

Tableau 2. Dissociation en demi-molécules par les électrolytes.

Dans tous les cas le tampon a été 0,08 M. en acétates et avec la composition: { 0,068 M-Na Ac / 0,012 M-H Ac }

Solution	Molarité de NaCl	Pourcentage des	
		Molécules entières	Demi-molécules
a Hémocyanine originale.	0,2	100	—
	0,4	71	29
	0,6	32	68
	0,8	26	74
	1,0	24	76
b Hémocyanine séparée: solution privée de son dépôt de protéine.	0,2	100	—
	0,45	61	39
	0,5	42	58
	0,6	16	84
	0,65	10	90
	0,8	—	100
	1,0	—	100
c Hémocyanine séparée: solution du dépôt de protéine.	0,2	100	—
	0,6	56	44
	0,8	49	51
	1,0	52	48

d'électrolyte de molarité 0,28, l'analyse par l'ultracentrifuge ne révèle dans les deux cas qu'un seul composant avec une constante de sédimentation correspondant à l'hémocyanine originale non dissociée. Mais ce composant montre des propriétés de dissociation différentes, selon qu'il provienne de la solution *b* ou de la solution *c*. Les résultats de dissociation en fonction de la concentration de l'électrolyte sont donnés dans le tableau 2 et la figure 1. Nous donnons en même temps les résultats pour l'hémocyanine originale non-séparée.

Le tableau 2 et la figure 1 nous montrent que l'hémocyanine de la solution *b* est plus dissociée que l'hémocyanine originale (*a*) et que celle de la solution *c*. Quand la concen-

tration des électrolytes est plus grande que 0,8 M, la solution *b* est complètement dissociée en demi-molécules, et la solution *c* contient des molécules entières et des demi-molécules dans la même proportion qu'avant la réassociation.

Nous avons ainsi obtenu deux solutions d'hémocyanines de propriétés différentes quant à l'influence des sels: une où l'hémocyanine peut être complètement dissociée en demi-molécules et une où la dissociation maxima est inférieure à celle de l'hémocyanine originale. Les expériences de séparation semblent donc vérifier l'hypothèse de la coexistence de deux espèces de molécules.

Molécules croisées.

Les recherches de Svedberg et Heyroth (7) et de Eriksson-Quensel et Svedberg (8) ont montré que l'hémocyanine de *Helix pomatia* est dissociée en huitièmes, si le pH de la solution est porté à un pH entre 8,0 et 9,5. En dialysant la solution alcaline contre une solution neutre, les fragments de dissociation s'associent, en donnant des molécules ayant une constante de sédimentation égale à celle de l'hémocyanine originale non-dissociée. La réassociation des huitièmes a lieu complètement pour certaines solutions d'hémocyanine, tandis qu'elle n'a lieu que partiellement pour d'autres solutions, bien que les précautions prises soient les mêmes. En général, il faut, pour que la réaction soit réversible, que l'hémocyanine ne soit gardée dans le milieu alcalin que 10 heures au maximum et que le pH de la solution ne dépasse pas 8,5. Dans ce qui suit, nous n'avons étudié que des solutions où la réassociation des huitièmes était complète.

Tiselius et Horsfall (9) ont obtenu des molécules croisées entre *Helix pomatia* et *Helix nemoralis*. Une solution d'hémocyanine contenant les deux hémocyanines était portée au pH 8,5 où toutes les deux sont dissociées en huitièmes. La réassociation avait lieu en portant la solution au pH 6,8. La mobilité électrophorétique de l'hémocyanine ainsi obtenue a une valeur qui se trouve entre celle de l'hémocyanine de *Helix pomatia* et celle de *Helix nemoralis*.

Si l'hémocyanine de *Helix pomatia* contient deux espèces de molécules A et B, nous devons obtenir des molécules croisées

quand une solution, ne contenant que des huitièmes, est portée à un pH où la réassociation a lieu. Nous appelons α les huitièmes provenant de A, et β ceux de B. Quand la réassociation a eu lieu, nous devons avoir, en plus des deux molécules originales A et B, sept autres espèces de molécules. La probabilité de formation de ces neuf différentes hémocyanines est donnée dans le tableau 3.

Tableau 3. Probabilité de formation des différentes hémocyanines réassociées.

α = huitième provenant de A
β = » » de B

Nous supposons que la concentration de A soit 75 p. c.

Molécule contenant	Probabilité de formation	
8 α = A	0,10011	
7 α, 1 β	0,26697	
6 α, 2 β	0,31146	
5 α, 3 β	0,20764	
4 α, 4 β	0,08652	
3 α, 5 β	0,02307	
2 α, 6 β	0,00384	0,11382
1 α, 7 β	0,00037	
8 β = B	0,00002	

Une solution d'hémocyanine qui ne contient que des huitièmes (pH = 8,3) a été portée à pH 5,3, la concentration des électrolytes étant 0,28 M. A première vue il n'y a pas de changement: l'analyse à l'ultracentrifuge donne un seul composant ayant une constante de sédimentation égale à celle de l'hémocyanine originale non-dissociée. Mais, comme nous devons nous y attendre, s'il existe à l'origine vraiment deux espèces de molécules A et B, les propriétés de dissociation de l'hémocyanine réassociée sont différentes de celles de l'hémocyanine originale. La dissociation par les sels a été étudiée dans une solution qui était 1,0 M en NaCl et 0,08 M en tampon d'acétates. L'hémocyanine réassociée est plus dissociée que l'hémocyanine

Tableau 4. Dissociation maxima de l'hémocyanine originale et de l'hémocyanine réassociée.

Solvant: 1,00 M-NaCl et 0,08 M tampon d'acétates. pH = 5,2.

Solution	Pourcentage des	
	Molécules entières	Demi-molécules
Hémocyanine originale	25[1]	75
Hémocyanine réassociée	9	91
	10	90
	14	86
	12	88
	13	87

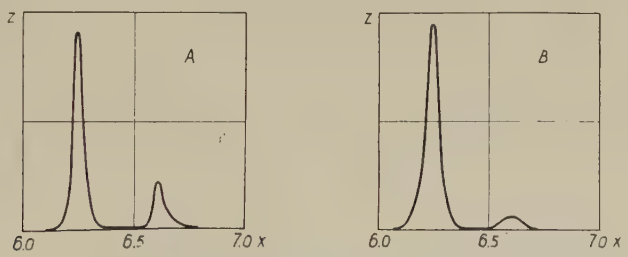

Fig. 3. Diagrammes de sédimentation montrant la dissociation maxima en demi-molécules par les sels.

A: L'hémocyanine originale. Solvant: 1,00 M-NaCl et 0,08 M tampon d'acétates. pH = 5,2.

B: L'hémocyanine réassociée après dissociation en huitièmes. Même solvant que A.

Force centrifuge 120 000 fois la force de la pesanteur; temps après avoir atteint pleine vitesse 40 min. pour A et 45 min. pour B.

originale. Les résultats sont donnés dans le tableau 4 et la figure 3.

La détermination de la relation du pourcentage de l'hémocyanine dissociée et non-dissociée est très incertaine quand un des composants apparait en faible concentration. En comparant les valeurs des probabilités du tableau 3 avec les résultats du

[1] Cette valeur est une valeur moyenne de 15 déterminations qui se sont trouvées entre 22 et 29.

tableau 4, il semble néanmoins certain qu'une molécule d'hémocyanine réassociée doit contenir au moins quatre huitièmes β, pour qu'elle ne subisse pas la dissociation par les sels. Il est possible que les fragments β puissent occuper de telles positions qu'une molécule contenant quatre β est dissociée par les électrolytes. La détermination de la concentration est malheureusement trop incertaine pour permettre une analyse approfondie.

Comparaison avec d'autres hémocyanines.

L'influence des électrolytes sur la dissociation a été étudiée surtout pour *Helix pomatia* mais aussi pour quelques autres gastropodes. Nous donnons ici quelques résultats préliminaires. Ainsi l'hémocyanine de *Helix hortensis* rapelle celle de *Helix pomatia*: elle est partiellement dissociée en demi-molécules par l'addition d'un électrolyte. La dissociation maxima (qui est environ 30 p. c.) est pourtant inférieure à celle de *Helix pomatia*. L'hémocyanine de *Helix arbustorum* est complètement dissociée en demi-molécules par les électrolytes: elle a donc les propriétés de dissociation de l'espèce A de *Helix pomatia*. L'hémocyanine de *Paludina vivipara* n'est pas dissociée par les électrolytes mais bien par la variation du pH (10, 11): elle a donc les propriétés de dissociation de l'espèce B de *Helix pomatia*.

Les constantes de sédimentation et la stabilité en fonction du pH ont été utilisées par Svedberg et ses collaborateurs pour caractériser les diverses hémocyanines (12, 8). Nous avons vu que la dissociation par les électrolytes diffère considérablement pour les quatre hémocyanines étudiées (*H. pomatia*, *H. hortensis*, *H. arbustorum* et *Paludina vivipara*). Il y a là une autre possibilité de classification qui pourra être utile dans les recherches biologiques.

Résumé.

1. Par des expériences de séparation dans une centrifuge préparative, nous avons obtenu deux solutions d'hémocyanines: une subissant la complète dissociation en demi-molécules par les électrolytes et une étant moins dissociée que l'hémocyanine originale dont la dissociation maxima est de 75 p. c.

Ces résultats confirment l'hypothèse que l'hémocyanine de *Helix pomatia* est composée de deux espèces de molécules.

2. Par réassociation des huitièmes, nous avons obtenu une hémocyanine dont la dissociation par les électrolytes est plus grande que celle de l'hémocyanine avant dissociation. Ce changement trouve son explication en supposant deux espèces de molécules pour l'hémocyanine originale.
3. Parmi les gastropodes, nous avons trouvé des hémocyanines qui sont complètement, partiellement et pas du tout dissociées en demi-molécules par l'addition d'un électrolyte.

Les frais de recherche ont été en partie défrayés par le Fonds Nobel de Chimie et la Fondation Rockefeller.

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On the Fermentation of Cellulose and Similar Carbohydrates by Thermophilic Bacteria.

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The *thermophilic bacteria*, whose activities can be displayed at temperatures higher than the coagulation points of many proteins, constitute a group which is interesting from both the scientific and the technical points of view. It appears, however, to have been but little investigated as a whole, even though certain types of bacteria belonging to it have been studied more in detail. Among the latter may be mentioned particular forms which decompose cellulose and noxious bacteria in food substances. Pathogenic thermophiles are probably unknown.

Thermophilic Cellulose Fermentation.

By thermophilic cellulose fermentation is to be understood in the following account an anoxidative decomposition of cellulose owing to the activity of obligate and facultative anaerobic thermophilic bacteria at about 60° C (cf. p. 442). In natural material, however, the cellulose-fermenting bacteria attack also other resistant high molecular carbohydrates (hemicellulose) at the same time as the cellulose, and in certain cases also more readily fermentable substances (starch, pectin, sugars). Cellulose fermentation of plant material therefore implies, in the first place, the conversion of its chemically and biologically relatively resistant polysaccharides, which are usually the main product of the plant tissue. The products in the fermentation of cellulose or a natural mixture of polysaccharides are alcohols and organic acids.

Owing to the cheapness and abundance of the native cellulose material, the technical utilization of cellulose fermentation is an important problem, which, however, is still unsolved, although thermophilic cellulose fermentation has been known for nearly fifty years and has constituted a field for extensive research work in various countries.

With regard to the abundant literature, reference should be made to the reviews by, *inter alia*, Coolhaas (1), Simola (2) and Tetrault (3) (up to 1930) and by R. Meyer (4) (up to 1938). Since 1938 it appears that chiefly Russian research workers have studied cellulose fermentation; the majority of their works are comprised in "*Mikrobiologija*".

In connection with attempts to ferment cellulose by means of elective cultures from soil and compost Enebo (5) found besides, the "obligate"[1] cellulose-fermenting types of bacteria, which were first isolated and described by Snieszko (6), also strains which had the capacity to convert both sugars and cellulose, and also some strains of non-cellulose-fermenting thermophilic soil bacteria. Certain of the latter had a symbiotic relationship with the "obligate" cellulose-fermenting strains, and this rendered attempts at isolation very difficult. Enebo's investigation resulted in, *inter alia*, a proposal for a simple classification of thermophilic cellulose fermenting bacteria, which had not been available previously (7). In this classification, which is based on physiological distinctions, all the known forms of such bacteria can be fitted quite naturally (see p. 442).

Some Questions Concerning Thermophilic Bacteria.

The designation thermophilic is applied to such bacteria as only grow within a temperature interval of c. 40—75° C, with a growth optimum at c. 60°. At times an upper limit of 80° is described. Far more important, however, is the lower temperature limit, for even though this may be between 40 and 45° C and even higher in the laboratory environment, it is open to discussion whether, in view of the natural occurrence and the conditions of life of the thermophilic bacteria, they

[1] As regards the designation "obligate" in this connection, see p. 442.

should not in general be termed heat-tolerant instead of thermophilic.

In the first comprehensive work on thermophilic bacteria (1888), GLOBIG (8), on investigating 12 strains, found the greatest temperature interval to be 15—68° C and the least 54—65°. In answer to the question how bacteria with such a high vegetation temperature as in the last-mentioned case could normally occur in the top layer of soil, GLOBIG suggested the warming of the surface of the earth by solar radiation during the summer; he could give no experimental proof for this, however. As thermophilic bacteria are particularly abundant in the tropics, this circumstance certainly plays some part (DE KRUYFF, 9). In temperate zones, however, the soil is seldom heated to 50—60° C, at least not in the humid condition which is necessary for the growth of bacteria.

The solution of the problem of the general and abundant occurrence of thermophilic bacteria together with mesophilic bacteria was given in principle as early as in 1895 by RABINOWITSCH (10), who showed that bacteria which were obligate thermophiles on one medium could grow on another at lower temperatures, certainly at a reduced rate of growth, but otherwise quite normally. In more recent times the same question has been dealt with by HANSEN (11), who determined the generation period for a thermophilic bacteria as 16 minutes at 54.5° C and 370 minutes at 20° C. Thus in laboratory experiments thermophilic bacteria can multiply at moderate temperatures. RABINOWITSCH also established the fact that such bacteria are normally developed in the alimentary canals of herbivorous animals, which appear to present a specially suitable environment. With manure, therefore, the thermophilic bacteria are spread over arable and garden soil, where they occur more abundantly than, for example, in forest soil. Thus MISCHUSTIN (12) used the number of thermophilic bacteria in different soils as a measure of cultivation. In unworked soil the number of thermophilic bacteria per gram of the surface layer was only 1 000 as against 100 000—380 000 in soil in a good state of cultivation. The larger number of bacteria in the latter case was considered to be partly due to manuring with stable manure.

Thus while an explanation was early found of the fact that thermophilic bacteria normally form part of the bacteria flora of the soil over the greater part of the globe, the reason why these bacteria thrive at high temperatures is still obscure. RABINOWITSCH assumed that the heat-tolerance was an adaptation. Spores of several generally occurring mesophilic bacteria exhibit such tolerance to high temperatures, without the resistance to heat appearing to be conditioned by adaptation. Thus, as is

well known, the spores of *Bac. subtilis* endure boiling for at least 1 hour. Corresponding unfavourable conditions will hardly be met with in nature, except in the case of the self-heating of grass in compact heaps, and so on, phenomena which are entirely without importance for the subsistence of Bac. subtilis. In this event, therefore, the heat-resistance will probably be a secondary effect; it is conceivable that the condition is the same in the case of both the vegetative forms and the spores of the thermophilic bacteria. In this connection it may be remarked that JANCKE (13) succeeded in making strains of *Bac. mesentericus* grow at 60° C, and obtained *mesentericus* strains from a culture of thermophilic bacteria from milk. JANCKE therefore considered his thermophiles to be heat-resistant modifications of *Bac. mesentericus*.

The thermophilic cellulose-fermenting bacteria occur abundantly in the alimentary canals of ruminants, and thus, side by side with more or less mesophilic types, play a decisive role in the decomposition of the cellulose content of the fodder. In the digestive juices of warm-blooded animals there is no cellulase, so that the cooperation of cellulose-decomposing bacteria is a necessity for the digestibility of the cellulose. In the different groups of animals the cellulose decomposition takes place in different parts of the alimentary canal; in the horse it appears to occur chiefly in the caecum, in ruminants in the rumen. This decomposition proceeds with great intensity, in spite of the relatively low temperature, which must be due to the bacteria finding better conditions here than in the case of ordinary cellulose fermentation in vitro.

Different Types of Thermophilic Cellulose-Fermenting Bacteria.

In the fermentations which provided the basis for the characterization of the Groups A and C in ENEBO's classification (p. 442) the following medium (according to SIMOLA) was used:

$(NH_4)_2SO_4$	2.0 g
K_2HPO_4	1.0 »
$MgSO_4$, 7 H_2O	0.5 »
NaCl	0.5 »
LIEBIG's Meat Extract	1.0 »
(or, alternatively, Marmite Yeast extract)	2.0 »
Cellulose	20.0 »
Precipitated chalk	20.0 »
Tap water	1 000 ml.

The cellulose consisted in general of thin crêpe paper, which is more easily attacked by cellulose-fermenting bacteria than filter paper and remains better suspended in the solution. The crêpe paper contained 89 per cent of α-cellulose. In the case of sugar fermentations, only 10.0 g of cellulose and 20.0 g of sugar per litre of the culture medium were added. In this case the cellulose served as a carrier for the bacteria and was not attacked as a rule. In occasional cases, however, sugar fermentation took place first, and thereafter cellulose fermentation.

In the case of cellulose and sugar fermentations with bacteria belonging to Group B in the classification, Rotmistrov (14) employed a nutrient solution according to Viljoen, Fred and Peterson, which in principle was of the same kind as the above-mentioned.

As "obligate" cellulose-converting bacteria belonging to Group A sometimes probably ferment sugars on specially favourable media, the classification refers only to the conditions of the cellulose bacteria in laboratory experiments employing a nutrient solution of the same type as that described above (in which sugar will not be attacked).

Classification of Thermophilic Cellulose Fermenting Bacteria According to Enebo (5).

Group A. Obligatorily anaerobic, ferment chiefly cellulose, do not grow on the usual non-cellulose-containing media, produce butyric but not lactic acid. Do not form distinct colonies on agar media containing cellulose or starch.

Types of bacteria which may be placed in Group A have been described by Snieszko (6), Imschenetzkij (15), Pochon (16) and Enebo (7).

Group B. Aerophobic, ferment cellulose and starch and also sugars, produce butyric and lactic acids, form colonies on potato agar (non-cellulose-containing).

Group B has been isolated by Rotmistrov (14).

Group C. Facultatively aerobic, ferment sugars vigorously, cellulose slowly, grow on the usual non-cellulose-containing media, produce lactic but not butyric acid.

Group C has been isolated by Enebo (5).

Table 1. Amounts of Products and C-Balance for Some Thermophilic Fermentations (Enebo, 5).

Products formed	I Cellulose fermentation with mixed culture from compost. Temp. 60°		II Cellulose fermentation with bacteria of Group A. Temp. 60°		III Glucose fermentation with bacteria of Group D. Temp. 70°		IV Glucose fermentation with bacteria of Group D. Temp. 55°	
	g per 50 ml medium	gram atoms C per 50 ml medium	g per 50 ml medium	gram atoms C per 50 ml medium	g per 50 ml medium	gram atoms C per 50 ml medium	g per 50 ml medium	gram atoms C per 50 ml medium
	$\times 10^{-2}$	$\times 10^{-4}$	$\times 10^{-2}$	$\times 10^{-4}$	$\times 10^{-2}$	$\times 10^{-4}$	$\times 10^{-2}$	$\times 10^{-4}$
Ethanol	4.72	20.5	3.86	16.7	6.64	28.8	4.21	18.2
Butanol	0	0	2.99	16.2	0	0	0	0
Formic acid	1.96	4.3	0.41	0.9	6.53	14.2	5.22	11.3
Acetic acid	8.73	29.1	7.49	24.9	2.99	10.0	2.14	7.1
Butyric acid	7.44	34.8	13.48	61.2	0	0	0	0
Lactic acid	45.90	152.8	1.67	5.6	49.45	164.7	79.90	248.1
CO_2	17.47	39.7	23.81	54.1	1.65	3.8	3.52	8.0
Reducing substances expressed as glucose	5.26	17.5	0	0	—	—	—	—
Total	91.48	298.7	53.71	179.6	67.26	221.5	94.99	292.7
C in inoculation culture	—	12.8	—	12.3	—	15.5	—	15.5
C in products	—	285.9	—	167.3	—	206.0	—	277.2
C in added carbohydrate	—	348.7	—	345.5	—	318.3	—	318.3
C in remaining carbohydrate	—	46.2	—	169.0	—	105.0	—	25.1
C in consumed carbohydrate	—	302.5	—	176.5	—	213.3	—	293.2
% found	94.5		94.8		96.6		94.5	

With Group C is associated a Group D with analogous properties, with the exception of the capacity to ferment cellulose. Various kinds of sugars, both pentoses and hexoses, are fermented vigorously. Group D has probably been observed earlier, as it is easy to prove and isolate; it is important as a symbiont in elective cultures containing Group A.

The most vigorous cellulose-fermenting bacteria probably belong to Group A. In elective culture they can be cultivated without any special anaerobic technique being necessary. It is very difficult to isolate them, owing to their tendency to symbiosis with other thermophilic soil bacteria. The function of the latter in symbiosis culture has hardly been ascertained, but it may be assumed that it consists in lowering the redox potential of the nutrient solution, removing inhibiting intermediate products in fermentation, and providing the cellulose bacteria with organic N-compounds. Snieszko (6) worked out a method for preparing pure cultures of the cellulose-fermenting bacteria, in which live yeast was used to lower the redox potential. Imschenetzkij (15) has focussed his attention particularly on the last-mentioned of the hypothetical functions of the symbionts and endeavoured to stimulate the pure cultures by the addition of faecal extract. In Enebo's experiments, after a number of failures, some pure cultures were finally obtained by Snieszko's method. These cultures rapidly degenerated, however, in spite of anaerobic cultivation and the addition of, *inter alia*, faecal extract, so that no experiments, beyond the determination of their purity, could be carried out. In mixed culture with Group D the anerobic cellulose-fermenting bacteria exhibited unlimited vitality, however. These mixed cultures were superior to the elective cultures, in fermenting celluloses of different kinds rapidly.

As an example of what products may be formed in thermophilic cellulose and sugar fermentation and their relative amounts, some results are adduced below.

In this connection it may be mentioned that several authors using elective cultures (Viljoen, Fred and Peterson (17), Scott, Fred and Peterson (18), Sarles, Fred and Peterson (19) and others), or employing pure cultures (Snieszko (6)), only obtained ethanol, acetic acid and butyric acid as non-gaseous products, which indicates that in these cases Group A predominated or was present in pure form. In experiment II in the above table the culture contained Groups A and C, the

former strongly predominant; it is very probable that formic acid and lactic acid derived from Group C.

The analyses which are the basis of all the figures in the present work were made according to the methods generally used in the case of such fermentations. The alcohols were distilled off and oxidised to the corresponding acids by means of bichromate and H_2SO_4. After two steam-distillations (the second being carried out in a micro-apparatus after the neutralised acid mixture had been evaporated to a small volume), the acids were determined by means of WERKMAN's partition method employing isopropyl ether. The oxidation entails certain small losses, for which corrections have been introduced. Further, the butanol is converted into a mixture of butyric acid and acetic acid. Acetic acid and butyric acid are determined after steam-distillation as above, formic acid by oxidation with $HgCl_2$, and lactic acid by oxidation to acetic acid according to SZEBERENYI. (For a detailed description reference should be made to ENEBO (20)). The C-balances in the table show that the methods of analysis used give satisfactory results. A quicker method of analysis is, however, very desirable. TISELIUS' adsorption method (21) may perhaps be used for the determination of the acids.

Some Technical Aspects of Thermophilic Cellulose Fermentation.

Two circumstances in particular have hitherto placed obstacles in the way of the technical exploitation of cellulose fermentation. The first is the low concentrations at which the fermentation products are obtained, the other that the cellulose-fermenting bacteria require a material in which the cellulose is not accompanied by all too great quantities of incrusting substances. Thus native wood cellulose is not fermentable without special preparation to remove the lignin (OLSON, PETERSON and SHERRARD, 22).

In laboratory experiments it has proved that the medium should not contain more than c. 3—4 per cent of cellulose, if the latter is to be entirely fermented. The accumulation of fermentation products appears to check fermentation even at the relatively low concentration which corresponds to 2—3 per cent of cellulose. The immediate cause of the obstruction is still unknown. As in such experiments provision is gener-

ally made by the addition of $CaCO_3$ or $MgCO_3$ for the successive neutralisation of the acids formed, the obstruction cannot be due to a lowering of the pH.

For the sugar-fermenting Group D (see above) the conditions are analagous, in that 2—3 per cent of sugar in the medium is the largest amount that can be fermented. We have inoculated solutions, containing up to 10 per cent of sugar, with Group D and obtained normal fermentation, independently of the sugar concentration. In all cases, however, fermentation ceased as soon as 2—3 g of sugar per 100 ml had been fermented. With the addition of $CaCO_3$ a final pH of c. 6 was obtained, while the pH in unbuffered sugar solution fell to c. 4.5 before fermentation ceased.

In the case of cellulose fermentation in the alimentary canals of herbivorous animals the fermentation products can be removed, shortly after they are formed, by means of diffusion and bacterial activity. Diffusion through the walls of the stomach or intestines may play a specially important rôle. In view of the provable nutritive value of cellulose (e. g. fodder cellulose) the question has been raised whether in this case its decomposition proceeds as far as to acetic and butyric acid, which have little nutrient value. Possibly here, as also at times in laboratory experiments, a certain amount of glucose accumulates, which is to some extent absorbed by the walls of the stomach or intestines so quickly that it is removed from the activity of other bacteria. (We shall have occasion to return later to the question of the reaction of the cellulose-fermenting bacteria to glucose.) In view of the considerable difference in speed between the decomposition of cellulose in animal organisms and in vitro in laboratory experiments, it may be supposed that the more rapid conversion in the former case is, at least partly, an effect of the successive removal of the fermentation products.

In an attempt to ascertain to what extent the quantitatively most important fermentation products have an inhibiting effect at higher concentrations, we have carried out a series of fermentations with a pure culture of a facultative aerobic sugar-fermenting bacterium belonging to Group D in the proposed classification. As has previously been mentioned, the inhibiting effect

in this case appears to be analagous with that appearing in the case of cellulose fermentation. The bacterium used presented certain advantages as, in contradistinction to the available anaerobic cellulose-fermenting bacteria (Group A), it gave rise to vigorous fermentation even in pure culture. The fermentations were carried out in evacuated and sealed ampoules partly filled with glucose-cellulose substrate (p. 442), which were mixed with increasing amounts of ethanol, formic acid, acetic acid and lactic acid respectively, which comprised the chief products of the glucose fermentation. The object of the evacuation and sealing was to eliminate the effect of the air on the formic acid (Enebo, 5), besides which evaporation of ethanol was excluded. The volume of the ampules was c. 140 ml and the amount of medium 25 ml. The original glucose content was 10 g/litre. The quantity of culture used for inoculation was 5 per cent of the volume of medium.

Table 2.

	Amount of Ca salts added, g/litre			
	5.0	10.0	20.0	30.0
a) *The effect of Ca salts of formic, acetic and lactic acid on glucose fermentation. Residual sugar, 7 days after inoculation.*				
Residual sugar, g/litre, with:				
Ca formate	2.4	5.9	7.4	7.8
Ca acetate	0.1	—	2.9	4.6
Ca lactate	0.1	0.3	1.1	2.8
Residual sugar, 11 days after inoculation.				
Residual sugar, g/litre, with:				
Ca formate	0.1	5.4	6.3	7.5
Ca acetate	0.0	0.1	2.1	4.0
Ca lactate	0.0	0.1	0.1	2.2

	Amount of ethanol added, g/litre				
	1.0	2.0	4.0	8.0	16.0
b) *The effect of added ethanol. Residual sugar, 11 days after inoculation.*					
Residual sugar, g/litre	0.0	0.0	0.0	0.0	1.1

The tables show that the three organic acids in the form of Ca salts exercised a clearly inhibiting effect, which was most pronounced in the cases where formate was added. This may indicate that the formate ion in considerable concentration is particulary unfavourable. It must, however, also be taken into account that the Ca ions may have a corresponding specific effect. According to LANGWELL (23) a content of Ca ions exceeding 4 g CaO per litre has an inhibiting effect on cellulose fermentation. Owing to the lower equivalent weight of the formate the solution came to contain 1.68 times as much Ca in the experiments in which formate was used as in those in which lactate was added. (12.9 g and 7.7 g CaO per litre respectively at the highest salt concentration). Finally we must observe that the retardation may also be entirely or partly a general ionic effect, in which the ionic strength of the solution will be decisive. On account of all this, the only conclusion that can be drawn from the above experiments is that the accumulation of acid fermentation products in the form of calcium salts in the medium checks fermentation; a more detailed explanation of this calls for a further investigation.

As appears from Table 2, the inhibiting effect of ethanol is inconsiderable. In view of the fact that relatively small amounts of ethanol are formed in fermentations, the effect of ethanol will probably be of no practical importance.

That the retardation is not specifically confined to fatty acids or Ca ions is shown by an experiment in glucose fermentation when considerable amounts of phosphate buffer were present. The phosphate mixture consisted of 32.5 % KH_2PO_4 and 67.5 % Na_2HPO_4, $2\,H_2O$.

Table 3. The Effect of Phosphate Admixture on Glucose Fermentation. Residual sugar, 12 days after inoculation. Original glucose content 20.0 g/litre.

	Phosphate admixture g/litre		
	10.0	20.0	25.0
Residual sugar, g/litre	5.4	15.6	17.8

It would be a great improvement if during fermentation the inhibiting compounds, i. e. in the first place the acids, could be removed successively in such a way that bacterial activity was not decreased. This would imply that a larger

amount of cellulose than otherwise in a certain volume of mash could be fermented. For such a procedure to be of any technical importance it is necessary that, at the same time as they are removed, the acids can be concentrated to some extent.

The precipitation of the acids as insoluble metal salts is not feasible in practice, because the salts of the metals which technically could be considered in this case are readily soluble. We have carried out some preliminary experiments with anion exchangers (of the resinous type). It was found that the latter could be present during fermentation and take up the acids satisfactorily. Owing to the low exchange capacity of such material, however, the method is of no technical value at the present time.

As these methods for the successive removal of products during the actual fermentation are not technically feasible at present, the fermentation must be allowed to proceed until the accumulation of acids in the mash results in a retardation. In this connection the composition of the mixture of products and the concentration of the products in the fermented mash will be of the greatest importance in the working up.

As extreme cases in respect of the relative quantities of the products the following values may be cited:

	I	II
	Langwell (23)	Veldhuis, Christensen[1] and Fulmer (24)
Ethanol, g/litre	0.43	7.9
Acetic acid »	20.8	7.8
Butyric acid »	2.12	0.37

A mash abundant in alcohol according to II, with about the same ethanol content as in fermented sulphite lye, is

[1] These values were obtained for 3 g of cellulose/100 g of nutrient solution. Veldhuis et al. indicate, however, that the ethanol formation was independent of the cellulose concentration within the range 2—5 g cellulose/100 g nutrient solution, so that the highest ethanol content in their experiments must have amounted to c. 13 g/litre.

naturally most simply worked up by distillation. The cost of this corresponds to that of distilling in the manufacture of sulphite spirit. It is uncertain whether the acids can be economically recovered on an industrial scale.

Langwell's mash is an example of the opposite extreme. Depending on the procedure, either only the acids, or both the acids and the alcohol, can be recovered economically. The latter may be the case after concentration by freezing out the water according to a method worked out by Öman. (A short description is given in 25).

In this continuous concentration by freezing, the ice is collected on the surface of the solution on a level with the edge of the freezing tank, washed there with the basic solution or with water and removed. The concentrated solution is taken out at the bottom of the tank. When dilute solutions of Ca salts of lower fatty acids are treated by the freezing method, the ice is separated off until the solution has become so concentrated that the eutectic is nearly reached, which corresponds to a relatively high salt content in the solution. Freezing is now discontinued and the concentrated salt solution is treated further by evaporation.

As has been mentioned, mash from cellulose fermentations contains chiefly acetic acid, butyric acid and ethanol, and further, at times, formic acid, and probably also small quantities of valeric acid. That it is possible to recover economically the first three acids mentioned on an industrial scale by the freezing method is clear from a consideration of their solubility relationships. The following solubility values (according to Lumsden, 26), referring to g anhydrous salt/100 g water, are of interest in this connection:

	0°	10°	20°
Ca formate	16.15	16.37	16.60
Ca acetate, $2\,H_2O$	37.40	35.98	34.73
Ca butyrate, $1\,H_2O$	20.31	19.15	18.20

In all cases the solubility is fairly independent of the temperature.

According to Guthrie (27) the cryohydric point for Ca acetate lies at -11.8° C. Rectilinear extrapolation of Lumsden's solubility curve to this temperature gives somewhat more than 39 g of

Ca acetate (anhydrous) in the cryohydrate per 100 g of water. We have determined the freezing curve between 0° and −10°. Its intersection with the extrapolated solubility curve tallied with GUTHRIE's value to within about one-tenth of a degree. The freezing-out of pure Ca acetate solution can therefore probably be forced up to about 35 g salt/100 g water, i. e. a c. 26 per cent solution.

It would be beyond the scope of the present account to enter upon a detailed estimate here of the cost of producing concentrated acetic acid from, for example, a 3 per cent Ca acetate solution, but a rough estimate suggests that in this country before the war a total cost of about 200 Swedish crowns per ton of 100 per cent acid could be reckoned with, provided that the process was carried out on a large scale. The cost of the actual concentration by the freezing method would probably amount to only half that amount. The remainder would comprise the costs of any necessary evaporation, sulphuric acid admixture and distillation. The calculations have been based on the following prices: electric power 0.02 crowns per kWh, steam 4 crowns per ton and sulphuric acid 100 crowns per ton.

An acetic acid-ethanol mash could probably also be worked up in this way, provided that the initial concentration were not too low. Ethanol is concentrated by freezing to the same degree as the salts, and can then be recovered by distillation.

In view of the above considerations, the recovery of the products from thermophilic cellulose fermentation on an industrial scale does not appear to be economically impossible. In favourable cases, as in the two above examples, the expenses of recovery are so low that other factors would be decisive in estimating the possibilities of the industrial utilization of this fermentation process. It must be taken into account, however, that LANGWELL's and VELDHUIS' experiments had unusually favourable results, and that in many cases fermentation ceases at considerably lower concentrations of the products.

Apart from the low concentration of the fermentation products in the mash, the reaction of the cellulose-fermenting bacteria to the cellulose-containing material which might be considered for industrial cellulose fermentations is of special technical importance. Briefly it may be said that the cellulose in the soft parts of plants and in annual plants is more easily converted on the whole than lignified material. Native wood cellulose especially is almost entirely resistant to cellulose-fermenting bacteria.

Olson, Peterson and Sherrard (22) have shown that a rather thorough treatment with the object of almost completely removing the lignin is necessary to make wood-flour of various kinds fermentable. The inhibiting effect of the lignin in such material appears to be due to its forming an intimate compound with the cellulose, which protects the cellulose molecules from the attacks of enzymes. For the cellulose to become fermentable it is not necessary that the lignin be entirely removed from the material, but chiefly that its compound with the cellulose be dissolved. According to Olson *et al.* free lignin in the form which can be extracted from wood does not check cellulose fermentation. Experiments in this laboratory (unpublished) by S. Ljungbo appear to show that the fermentability of different technical wood pulps, produced according to the sulphite or sulphate methods, does not seem to be inversely proportional to the lignin content in the pulp, but to be principally dependent on the degree to which the intimate compound between the cellulose and the lignin is dissolved.

In countries where large quantities of cellulose from annual plants are obtained as waste, the possibilities of industrial cellulose fermentation are therefore greater than in this country. In U. S. A. and Russia especially, attempts have been made to utilize agricultural waste (straw, sugar beet pulp, maize cobs, etc.) by means of cellulose fermentation. In general such material can be fairly easily fermented without preliminary treatment or after simple treatment. Langwell, who appears to have been the first to perceive the technical importance that cellulose fermentation might attain, indicates in one of his patents as suitable raw materials, apart from sulphite pulp, maize cobs, rice straw, fresh bamboo and fresh grass (23). By means of a simple preliminary treatment of non-lignified plant material with alkali the fermentability can be increased.

Apart from lignin, other constituents of the raw material may also influence the fermentation process. We have carried out some experiments with beet pulp, which show how the metabolism of the cellulose fermenting bacteria can be changed by an increased supply of biologically active substances. In these experiments two kinds of dried beet pulp, soaked pulp with 3.8 per cent saccharose, unsoaked with 46 per cent saccharose were used. The inoculation culture consisted of a mixed culture of Groups A and D. (A "obligate" cellulose-fermenting, D only sugar-fermenting in artificial nutrient medium (cf. p. 442)). The experimental conditions were, for the rest, analogous with those indicated by ENEBO (5).

With fermentation of unsoaked beet pulp the nutrient solution contained from the beginning nearly 0.9 g saccharose per 100 ml owing to the sugar content of the pulp.

Table 4.

	Beet pulp	
	Unsoaked	Soaked
Added beet pulp (dry substance) g/100 ml	1.87	1.84
Fermentation time, days	11	11
Fermentation products as percentage of amount of beet pulp added		
Ethanol	9.08	2.17
Butanol	0.30	0.22
Formic acid	2.48	2.68
Acetic acid	4.08	10.21
Butyric acid	4.75	6.17
Lactic acid	18.06	16.21
	38.75	37.61

In view of the manner in which Groups A and D behave when they are cultivated on artificial media, the results of the beet pulp fermentations are rather remarkable. It was to be expected that, with the unsoaked beet pulp, the activity of Group A would have been completely inhibited in the same way as when sugar is added to a cellulose fermentation in an artificial nutrient medium inoculated with corresponding mixed cultures of A and D. In this latter case even 0.5 per cent of sugar results in the complete absence of cellulose fermentation, or possibly in the com-

mencement of cellulose fermentation after about a week, after all the sugar has been used up by the mainly lactic acid-forming Group D (Sarles, Fred and Peterson, 19, Enebo 5). In the case of the unsoaked beet pulp, however, normal cellulose fermentation set in from the beginning and Group D did not ferment more vigorously than was the case with soaked beet pulp without sugar content, as appears from the amounts of lactic acid. Microscopical examination of preparations from the fermentations showed that in both cases Group A was strongly predominant.

Summary.

Some questions concerning thermophilic bacteria in general are discussed. The most important properties of the thermophilic cellulose-fermenting bacteria are pointed out in connection with the classification of such bacteria proposed by Enebo.

One of the factors which have constituted the greatest obstacle to the technical utilization of cellulose fermentation appears to be the low content of fermentation products in the fermented medium. Some experiments showed that, in the first place, the acid products (in the form of salts), even in fairly low concentrations, impede sugar fermentation. Conditions are probably analogous in the case of cellulose fermentation. This drawback does not in itself imply, however, that thermophilic cellulose fermentation cannot be utilized industrially. A rough estimate shows that under favourable conditions the cost of recovering fermentation products is relatively small. This may be the case for such fermentations as chiefly aim at the production of ethanol, when the ethanol concentration may be as high as that in the fermented waste liquor in sulphite pulp manufacture. It would appear possible to work up mashes with predominantly acid content by freezing out the water according to a method proposed by Öman. Ca salts of the three fatty acids chiefly formed in cellulose fermentation exhibit solubility relationships which are favourable to the freezing method.

In connection with the relationships of the cellulose bacteria with cellulose-containing materials of various kinds, an experiment is described which proves that cellulose bacteria

whose cellulose-fermenting activity on artificial cellulose media is completely inhibited by sugars, in a beet pulp medium can tolerate the presence of saccharose and show normal cellulose fermentation.

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Retention of Atoms of Maternal Origin in the Adult White Mouse.

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What percentage of the atoms present in the new-born organism is retained during the later phases of life and what percentage is inherited by the subsequent generations? An attempt was made to answer these questions by following the fate of the phosphorus atoms in the white mouse, radio-phosphorus being used as an indicator.

The phosphorus atoms present as constituents of different compounds in the body of the new-born animal are released successively from the compounds in which they are present. The phosphorus atoms thus released are either excreted or re-incorporated into various compounds present in the body, the latter process being much more frequent. Although, for the sake of simplicity, we speak of phosphorus atoms, practically no phosphorus atoms but only phosphate radicals are released from and built into such phosphorus compounds. The organism is supplied with phosphorus in the form of phosphate radicals and the phosphorus atoms adhere, as far as is known, to their partners throughout the numerous metabolic processes in which they participate.

The white mice used in the experiment were kept on the following diet. Wheat flour, oatmeal and a small amount of milk were administered, while on alternate days only Cooley's standard food was provided. Once a week, cabbage or lettuce was administered as well.

About 0.1 mg. of labelled sodium phosphate with an activity of a few microcuries was administered by subcutaneous in-

jection to a pregnant mouse. As a result of introducing radio-phosphorus into the organism of the pregnant mouse, we obtain offspring of which the phosphorus contents were labelled. A litter consisted of about 8 offspring having almost the same weight, as shown in Table 1.

Table 1. Weight of 6 New-born Offspring of a Mouse.

No.	Weight in g.	Relative activity
1	1.3	100
2	1.3	98.5
3	1.4	99.0
4	1.2	93.5
5	1.3	99.5
6	1.3	—

The radio-phosphorus contents of the offspring may therefore also be expected to be almost equal. This fact makes it possible to determine the total ^{32}P content of the offspring at any date by measuring the total activity of any member of the litter.

One offspring was killed shortly after birth and dissolved in concentrated nitric acid. The phosphorus content of a known aliquot of the solution was precipitated as magnesium ammonium phosphate. The precipitate was filtered through an aluminium dish of 1.1 cm diameter having a perforated bottom covered with filter paper. The dish containing the precipitate was then placed unter the Geiger counter. By comparing the activity of an offspring killed at a given date with the activity of another killed at a later date, it was possible to calculate what percentage of the phosphorus atoms of maternal origin was lost in the interval between the two dates.

All offspring were killed successively, dissolved, and treated in the way described above. The writer is much indebted to Mr. K. Zerahn for dissolving the mice and precipitating their phosphorus content. All offspring were killed and investigated within about three months. After the lapse of this time, the

activity of the phosphate precipitates had decreased so greatly that it could no longer be measured with sufficient accuracy. The activity of the first offspring was compared with that of the second, the activity of the second with that of the third, and so on.

The mouse obtains its ^{32}P content not only by birth, but also by lactation. In order to simplify the problem, to reduce the ^{32}P content of the offspring mainly to such ^{32}P as was obtained by birth, the active mother was replaced by an inactive mouse soon after gestation. As the replacement of the mother was not made immediately after the birth of the offspring, we actually measured the loss of ^{32}P acquired by birth plus the ^{32}P acquired by lactation in the interval between birth and replacement of the active mother by an inactive one, i. e. within a few days.

Results.

The results obtained are shown in the following tables.

Table 2.

Mother injected February 9. Date of gestation: February 18. Replacement of the active by an inactive mother: February 22. Experiment 1.

No. of offspring	Killed	Relative activity	Weight in gm.
1	22/2	100	3
2	3/3	82	7
3	16/3	73	15
4	30/3	48	18
5	13/4	41	25
6	13/5	40	23

Loss of ^{32}P in the course of 81 days: 60 per cent.

In about 3 months[1], a time sufficient for mice to reach

[1] If only the last two values in Tables 2 and 3 are considered the average loss of ^{32}P in 80 days works out at 57 per cent. If all mice killed in April, May and June are considered, the average loss is 56 per cent in 72 days.

Table 3.

Mother injected February 9. Date of gestation: February 16. Replacement of the active by an inactive mother: February 23.

Experiment 3.

No. of offspring	Killed	Relative activity	Weight in gm.
1	24/2	100	2.8
2	5/3	90	6.9
3	19/3	70	13
4	2/4	57	15
5	16/4	53	20
6	18/5	51	16
7	7/6	39	22

Loss of ^{32}P in the course of 103 days: 61 per cent.

adulthood, only about 60 per cent of the ^{32}P content of the mouse acquired by birth is thus eliminated. The phosphorus content of the new-born mouse is found to be about 4 mg, the amount of P excreted by the mouse in the course of three month about 1 g. The fact that nearly one half of the maternal phosphorus is retained in the body, in spite of the comparatively large amounts of phosphorus excreted by the mouse in the course of 3 months, is due mainly to the protection of a large proportion of the phosphorus of the bones against interchange with the phosphorus atoms in circulation. The uppermost atomic layers of the bone apatite crystals interchange easily with the phosphorus atoms of the plasma or the lymph; furthermore, a kind of »biological recrystallization» takes place, i. e. dissolution of some molecular apatite layers followed by new formation of such layers through crystallization. All these processes, however, do not affect, or affect only at a very slow rate, large parts of the bone apatite which thus retain their P atoms. During the formation of the skeleton, a large proportion of the ^{32}P atoms present in the organism will find their way into the bone apatite and be fixed there to a very appreciable extent during the time of the experiment (3 months) or even for the lifetime of the mouse.

When comparing the ^{32}P content of several rats injected simultaneously with labelled phosphate at different dates, it was found (Hevesy 1939) (1) that the ^{32}P, in so far as it was not excreted, accumulated to a very large extent in the skeleton. This fact is illustrated by the following table.

Table 4. Percentage ^{32}P Present in the Body Found in Some Organs of the Rat.

Organ	Time after which the rat was killed						
	½ hour	4 hours	10 days	20 days	30 days	50 days	98 days
Muscles	18.3	19.4	25.8	28.8	25.2	12.1	3.6
Carcass after removal of bones, muscles, blood and skin . . .	37.0	43.6	21.0	16.4	13.1	6.7	2.9
Bones	19.1	23.4	43.1	43.1	51.8	76.5	92.6

Furthermore, when comparing the specific activity (activity of 1 mg *P*) of the bone *P* with the specific activity of the plasma *P* of the rabbit in experiments where the activity of the plasma was kept at a constant level throughout, it was found (Hevesy *et al.* 1940) (2) that 74 per cent of the epiphysial *P* and 93 per cent of the diaphysial *P* of the tibia remained unchanged after 60 days. These facts illustrate the ability of the skeleton to prevent an interchange of a large part of its *P* atoms with the *P* atoms of the plasma, thus preventing an ultimate excretion of such atoms.

As the calcium atoms of the organism are found to a still higher percentage in the skeleton than the phosphorus atoms, the organism may be expected to retain the average calcium atom obtained by birth still more jealously than it does the maternal *P* atoms. Similar considerations may apply to the magnesium and fluorine content of the organism. The atoms of maternal origin of all other elements present in the organism, however, can to be expected to leave the body at a much higher rate than do the phosphorus atoms of maternal origin.

The Percentage of ^{32}P Transferred from One Generation to Another.

Some experiments were carried out in order to follow the fate of the ^{32}P administered to a mouse in the second and the third generation.

The phosphorus content[1] of the new-born mouse constitutes about 2.4 per cent of the mother's phosphorus content; consequently, we should expect to find about 2.4 per cent of the ^{32}P contained in the pregnant mother in each new-born mouse. Actually, only about $^1/_4$ of that amount is found when comparing the activity of a mouse of the third and the second generation. This finding is explained mainly by the fact that a large part of the ^{32}P content of the mother is to be found in the skeleton and, as a large part of this ^{32}P does not reach the circulation, it does not participate in the formation of the foetus. The foetus acquires its phosphorus content mainly from the food phosphorus and the phosphorus present in the soft tissues. The phosphorus present in the circulation has a much smaller ^{32}P content than the average phosphorus of the mother, a fact which results in a comparatively low ^{32}P content of the new-born mouse. The first generation contains labelled phosphorus only in the soft parts of the body and in a minor part of the skeleton, and this because it obtained its phosphorus content by subcutaneous injection and not by the much more intimate foetal processes. The ^{32}P content of the first generation is therefore not strictly comparable with that of the second generation. The ^{32}P contents of the second and the third generations may, however, be compared. We may expect this ratio to be equal to that which we would obtain on comparing the ^{32}P contents of mice of the third and fourth or of the fourth and fifth generations etc, since it is to be expected that the percentage of ^{32}P passed from the third to the fourth generation will be the same as that transferred from the second to the third generation, etc. This conclusion is important since it is almost impossible to follow the fate of ^{32}P through more than three generations of mice.

From the injection of labelled phosphate to a mouse in the

[1] The P content of a new-born mouse weighing 1.33 g (average value) amounts to 4.2 mg, while that of a mouse weighing 31.8 g to 177 mg.

last stage of pregnancy (first generation) to the birth of the fourth generation about 188 days elapse; this corresponds to 13 half life periods of radio-phosphorus. During this time, the activity administered to the first mouse has decreased to less than 1/8 000 of its original value. As the fourth generation may be expected to contain about 10^{-7} of the ^{32}P present in the first generation (apart from the radioactive decay), we may expect to find only about 10^{-11} of the radio-phosphorus administered to the first generation. The measurement of such a low percentage of radio-phosphorus administered would require the administration of 100 millicuries ^{32}P or more.

The phosphorus content of an adult mouse amounts to about 200 mg or to $4 \cdot 10^{21}$ atoms. As of the ^{32}P atoms present in a mouse only $^1/_2$ per cent are found in a mouse of the next generation, it is easy to show that the eleventh generation will no longer contain a single ^{32}P atom and thus no P atom at all which was present in the first generation.

This result illustrates strikingly the fact that the hereditary dispositions are entirely independent of any atomic community with the forefathers, these dispositions being determined exclusively by the faculty of the atoms and molecules to enter certain characteristic configurations. It is the pattern which matters and not the single brick.

Summary.

Labelled phosphate was administered to a pregnant mouse. Each offspring was found to contain almost the same amount of ^{32}P. By killing the various offspring at different dates and comparing their ^{32}P contents, we determined the amount of maternal phosphorus atoms present in offspring at different times.

Between birth and maturity, i. e. in the course of three months, the mouse lost about 60 per cent of the P atoms acquired by birth.

By breeding three generations of mice, to the first generation of which ^{32}P was administered, the passage of phosphorus atoms from one generation to the next was followed. 0.6 percent of the ^{32}P present at the birth of an offspring of the

second generation was found to be present in an offspring of the third generation. We might expect to obtain the same ratio between the ^{32}P content of the third and fourth generation, and so on.

Making this assumption, it can be shown that a mouse of the eleventh generation no longer contains a single phosphorus atom present in the first generation.

The writer wishes to express his hearty thanks to Professor Niels Bohr and Dr. Jens Nielsen, the directors of the institutes in which the experiments described in this note were performed.

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Sedimentationsgleichgewichte und molekulare Konstitution von Gelatinefraktionen.

Von Hans Mosimann und Rudolf Signer.

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Im Jahre 1930 publizierten Krishnamurti und Svedberg (1) eine Untersuchung über die Ultrazentrifugierung von Gelatinelösungen. Zum ersten Mal kam hier die Ultrazentrifuge zum Studium dieser klassischen Substanz der älteren Kolloidchemie zur Anwendung. Bei der Diskussion über den Lösungszustand der Gelatine gingen die Ansichten älterer Forscher stark auseinander. Die einen nahmen eine mizellare, andere eine molekulare Dispersion der gelösten Teilchen an. Krishnamurti und Svedberg konnten zeigen, dass die Gelatine besonders im Gebiet des isoelektrischen Punkts eine grosse Aggregationstendenz aufweist, dagegen in stärker sauren oder alkalischen Lösungen molekular dispergiert ist. Durch Sedimentationsgleichgewichte konnte ferner die starke Polydispersität der untersuchten Substanz festgestellt werden.

Das Viskositätsverhalten fraktionierter Gelatine liess erkennen, dass sich bei Wahl von Lösungsmitteln wie Formamid, wässerigen Lösungen, die 1-m an Thioharnstoff oder 4-m an Harnstoff waren, die Aggregationserscheinungen der Gelatine weitgehend unterdrücken liessen (2, 3). Es schien daher auch von Interesse, die Molekulargewichte und die Polydispersität von Fraktionen in diesen Lösungsmitteln mit Hilfe der Ultrazentrifuge zu bestimmen. Zu diesem Zwecke wurden zwei der Fraktionen untersucht, nämlich eine, die mit HF I und eine andere, die mit VI bezeichnet wurde. Die Herstellung und die Eigenschaften dieser Fraktionen sind in (3) beschrieben. HF I wurde aus der Lösung unabgebauter Gelatine in 4-m Harnstofflösung durch Zusatz von Alkohol gefällt. VI wurde

aus einem durch Kochen in Wasser abgebauten Sol derselben Gelatine ausgefällt. HF I stellt den höchstmolekularen Anteil dieser Handelsgelatine dar und VI ein Abbauprodukt mit niedrigerem Molekulargewicht.

Die folgende Tabelle enthält die Resultate der Sedimentationsgleichgewichtsversuche, die mit VI in 1-m Thioharnstofflösung erhalten wurden. Das Lösungsmittel war gleichzeitig noch 0,2-m an NaCl zur Aufhebung eventueller Ladungseffekte. Die Versuchstemperatur betrug überall 20° C.

Tabelle 1.

c in g/100 ml	Umdrehungen/min	M_w	M_z	β
0,452	10 000	15 600	18 900	0,6
0,810	10 000	16 400	18 100	0,4
0,810	12 000	16 600	18 200	0,4
	Mittelwerte	16 200	18 400	0,5

Die Ausführung und Berechnung derartiger Experimente ist in der Monographie von Svedberg und Pedersen über die Ultrazentrifuge beschrieben (4).

Die Tabelle 1 zeigt, dass die Molekulargewichte im verwendeten Konzentrationsgebiet von der Konzentration unabhängig sind. Dies bestätigt die Behauptung, es trete keine Aggregation zu Mizellen ein. M_w und M_z liegen einander ziemlich nahe. Dies zeigt, dass die angewendete Fraktionierung zu einer Substanz fast gleichgrosser Teilchen geführt hat. In der letzten Kolonne der Tabelle ist β eingetragen, ein Koeffizient, der zur Charakterisierung der Uneinheitlichkeit dient. Es wird hierbei eine ganz bestimmte Molekülgrössen-Verteilungsfunktion angenommen (5). β ist für eine monodisperse Substanz $= 0$ und wächst nach der Beziehung $M_w = M_z e^{-0,5\,\beta^2}$.

Im folgenden werden die experimentellen Daten einer Gleichgewichtseinstellung der Fraktion VI in extenso wiedergegeben. Auch aus dem geringen Gang der M_{wx} und M_{zx}-werte zeigt sich, dass die Substanz nahezu monodispers ist. Die M-werte

sind fast so konstant wie bei Stoffen, die als streng monodispers angesprochen werden. Vgl. Zentrifugenbuch.

Tabelle 2. 0,810 g VI in 100 ml Lösungsmittel. 10 000 Umdrehungen/Minute, part. spez. Vol. 0,685 (6) $\varrho = 1{,}028$.

x	Z	c	M_{wx}	M_{zx}
4,68	104	0,621	16 200	18 300
4,73	111	0,652	16 300	16 500
4,78	118	0,686	16 300	17 900
4,83	126	0,720	16 400	16 500
4,88	134	0,759	16 400	17 200
4,93	143	0,810	16 200	15 900
4,98	152	0,842	16 400	14 800
5,03	161	0,888	16 300	17 300
5,08	172	0,936	16 400	20 800
5,13	186	0,988	16 600	23 700
5,18	208	1,046	17 400	
			$M_w = 16\,400$	$18\,000 = M_z$

Es ist auf jeden Fall bemerkenswert, wie weitgehend bei der Herstellung der Fraktion VI durch eine einfache Ausfälloperation Moleküle gleicher Grösse ausgesondert wurden.

Die Fraktion HF I ist bei analoger Herstellung viel weniger einheitlich, wie man aus Tabelle 3 ersieht.

Tabelle 3.

c	Umdr/Min	M_w	M_z	β
0,817	5 000	89 500	149 300	1,0

M_w und M_z sind stark verschieden, und β weist den hohen Wert von 1,0 auf.

Es bestätigt sich hier die allgemeine Erfahrung, dass die Isolierung monodisperser Stoffe durch Fraktionierung immer schwieriger wird, je höher die Molekulargewichte sind (7, 8).

Dies findet seine Erklärung in den Löslichkeitseigenschaften der hochmolekularen Stoffe.

Die in Tabelle 3 enthaltenen Molekulargewichtswerte der Substanz HF I wurden ferner durch Messungen der Sedimentationsgeschwindigkeit und des Diffusionskoeffizienten bestätigt (unpublizierte Versuche). Ferner gaben Gleichgewichtseinstellungen in 4-m Harnstoff ein M_w von 89 200.

Bei der früheren Untersuchung (2, 3) der Viskosität, des Säurebindungsvermögens und anderer Eigenschaften der Gelatinefraktionen wurde die Vermutung ausgesprochen, dass sich ihre Molekulargewichte unterscheiden müssen. Die hier mitgeteilten Sedimentationsgleichgewichte bestätigen die damalige Auffassung. Darüber hinaus lassen sich jetzt aus den Molekulargewichten und den Säurebindungsaequivalenten interessante Schlüsse auf die Molekülkonstitution ziehen. Die früher ermittelten Aequivalentgewichte der Fraktionen finden sich in der Tabelle 4 zusammengestellt.

Tabelle 4.

Fraktion	Aequivalentgewicht
HF I	1 230 ± 50
VI	580 ± 20

Oben wurde ausgeführt, dass HF I und VI aus derselben Handelsgelatine erhalten wurden. Wir können das so ausdrücken, dass VI aus HF I durch hydrolytische Spaltung entstanden sei. Es stellt sich somit die Frage, wie sich die Zahl der freien säurebindenden Gruppen beim Abbau verändert hat. Diese Zahlen, die wir mit a bezeichnen, erhält man bei jeder Fraktion als den Quotienten von Molekular- und Aequivalentgewicht. Als Molekulargewichtswert dürfen wir hier aber weder M_w noch M_z verwenden, sondern wir müssen ein mit dem Aequivalentgewicht vergleichbares Zahlenmittel des Molekulargewichts M_n heranziehen. Ist die Verteilungsfunktion der Molekulargrössen in unseren Substanzen so, wie sie Lansing und Kraemer (5) annehmen, so können wir dieses Zahlenmittel M_n unmittelbar aus M_n und β berechnen. Für die Fraktion

VI, wo die Polydispersität ohnehin klein ist, kann der Fehler, den man bei einer Abweichung der wirklichen von der angenommenen Verteilung begeht, nur sehr gering sein. Für HF I mag zwar der Fehler grösser sein, doch wird dies die folgenden Betrachtungen nur unwesentlich beeinflussen. Bestimmt man also das Zahlenmittel des Molekulargewichts M_n für die beiden Fraktionen aus M_w und β, so erhält man folgende Werte:

Tabelle 5.

Substanz	M_n	a
HF I	55 500	45
VI	14 300	25

In dieser Tabelle sind auch die a-Werte, die Zahlen der säurebindenden Gruppen pro Molekül, eingetragen.

Die M_n der Fraktionen verhalten sich etwa wie 4 : 1, während das Verhältnis der Aequivalentgewichte nur wie 2 : 1 ist.

Wäre durch jede Spaltung einer Peptidbindung in HF I ein neues Spaltstück aufgetreten, so beliefe sich die Zahl der neugebildeten freien Aminogruppen auf

$$\frac{M_1}{M_2} - 1 \quad (M_1 \text{ und } M_2 = M_n \text{ für HF I resp. VI}).$$

(Eine analoge Betrachtung liesse sich natürlich für die –COOH-Gruppen durchführen, wenn das Basenbindungsvermögen der Fraktionen bekannt wäre). Bezeichnen ferner a_1 und a_2 die Zahl der freien Gruppen für HF I resp. VI, so erhalten wir a_2 zu

$$a_2 = \frac{a_1 + \frac{M_1}{M_2} - 1}{\frac{M_1}{M_2}} = (a_1 - 1)\frac{M_2}{M_1} + 1.$$

Beim Einsetzen der Zahlenwerte für M_1, M_2 und a_1 erhalten wir $a_2 = 13$. Experimentell wurde jedoch ein ungefähr doppelt so grosser Wert festgestellt, nämlich 25. Es kann folglich nicht jede Spaltung einer Peptidbindung ein neues Bruchstück

geliefert haben. Das setzt aber eine Netzstruktur des hochmolekularen Gelatinemoleküls voraus (vgl. Fig. 1). Bei der Abtrennung kleinerer Partikel aus einem solchen Gebilde, wie es etwa die punktierte Linie andeutet, müssen immer mehrere Peptidbindungen gesprengt werden.

Die Verzweigungsstellen in der Peptidkette sind auf Grund des Aminosäurenbestandes der Gelatine leicht denkbar, da ja eine grosse Anzahl Monoaminodikarbonsäuren und Diaminomonokarbonsäuren im Molekül vorkommen. Es soll nicht be-

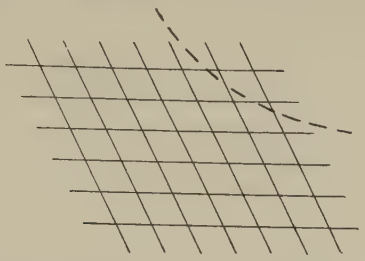

Fig. 1. Schematische Darstellung eines Netzmoleküls. Die punktierte Linie deutet die Abspaltung eines niedermolekularen Bruchstückes an, wobei es notwendig ist, mehrere Peptidbindungen zu sprengen.

hauptet werden, dass alle trifunktionellen Aminosäuren Verzweigungsstellen im Gelatinemolekül bilden. Das Bild soll einzig eine Idee geben, wie man sich ein solches Netz, das nach allen drei Dimensionen ausgedehnt sein kann, zu denken hat.

Werden immer mehr und mehr Peptidbindungen gesprengt, so müssen notgedrungen die niedermolekularen Fraktionen einfacher gebaut sein, und man erhält bei fortgesetzter Hydrolyse Abbauprodukte, die der Fig. 2 a oder 2 b entsprechen. Es sind entweder gerade Ketten oder verzweigte, aber nicht mehr vernetzte Moleküle.

Bei gegebenem Molekulargewicht und gegebenem Aminosäurenbestand ist das Säure-Basenbindungsvermögen *unabhängig* davon, ob die Moleküle geradkettig nach Fig. 2 a oder verzweigtkettig nach Figur 2 b gebaut sind. Zur Begründung dieser Behauptung sei nur ein einfaches Beispiel angeführt. Das Polypeptidmolekül bestehe aus vielen Monoaminomonokarbonsäuren und einer Diaminomonokarbonsäure. Es sei zuerst gemäss der Fig. 2 a konstituiert und die Diaminosäure befinde

sich irgendwo längs der Kette eingebaut. Das Molekül bindet zwei Aequivalente Säure, eines durch die Aminogruppe der endständigen Monoaminomonokarbonsäure und das zweite durch die freie basische Gruppe der peptidartig eingebauten Diaminosäure. Baut man nun ein verzweigtes Molekül mit den gleichen Aminosäuren, so ergibt sich folgendes. Die beiden basischen Gruppen der Diaminomonokarbonsäure werden bei der Verzweigung zu Peptidbindungen verbraucht. An zwei von den drei Kettenenden befinden sich nun aber freie basische

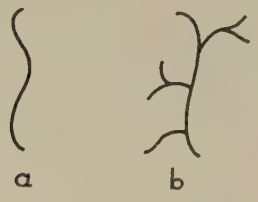

Fig. 2 a und 2 b. Gerad- oder verzweigtkettige niedermolekulare Polypeptidmoleküle, wie sie bei der Hydrolyse der hochmolekularen Gelatine entstehen.

Gruppen von Monoaminomonokarbonsäuren, so dass das Molekül auch wieder zwei Säureaequivalente binden kann. Analoge Betrachtungen führen zum Schluss, dass auch bei komplizierteren Molekülen die Verzweigungen ohne Einfluss auf die Säuren- und Basenbindung sind. Erst die Vernetzung führt zu einer Reduktion der sauren und basischen Gruppen.

Auf Grund dieser Überlegung lässt sich der Vernetzungsgrad der beiden Gelatinefraktionen ermitteln.

Die Analyse des Aminosäurenbestandes der Gelatine nach Waldschmidt—Leitz (9), ergänzt mit einigen neueren Bestimmungen durch Bergmann und Mitarbeiter (10), lehrt uns, dass 85,4 % des Ausgangsmaterials identifiziert werden konnten (berechnet als Anhydrid). Errechnet man das Durchschnittsmolekulargewicht eines Aminosäurenanhydrids unter Berücksichtigung der relativen Menge der vorhandenen Aminosäuren, so erhält man 101. Die Anhydride der Diaminomonokarbonsäuren, Arginin, Lysin und Histidin betragen resp. 8,2 %, 5,2 % und 0,8 % der Gelatine. Die Summe gibt 14,2 %. Arginin hat zwar 4 *N*-atome. Es hat sich aber gezeigt, (11, 12) dass Ar-

ginin mit zwei Molekülen Benzoylchlorid reagiert, wobei ein Benzoylrest in die Guanidingruppe, der andere in die α-ständige Aminogruppe eintritt. Man ist also berechtigt, Arginin wie eine Diaminomonokarbonsäure zu behandeln. Die Summe der drei Anhydride beträgt 16,7 % der bis heute identifizierten 85,4 % der Gelatinebausteine. Wie sich der Anteil bei einer vollständigen Erfassung des Aminosäurenbestandes verändern würde, entzieht sich unserer Kenntnis, und wir rechnen in Ermangelung besserer Zahlen mit 17 %.

Mit Hilfe des Durchschnittsmolekulargewichts der Aminosäurenanhydride ist es uns möglich erstens die Zahlen A der Aminosäuren in den Molekülen beider Fraktionen zu berechnen und zweitens die totale Anzahl der Aminogruppen B. Darunter verstehen wir die freien als auch die in den Peptidbindungen gebundenen Aminogruppen. Dieser Wert B muss ja um 17 % grösser sein als A. Wenn die Moleküle nicht vernetzt sind, gilt für die Zahl der säurebindenden Gruppen a folgende Beziehung:

$$a_{\text{ber.}} = B - A + 1.$$

Bei einer Vernetzung ist das berechnete a grösser, als das mit Hilfe der Säurebindung beobachtete.

Die Tabelle 6 gibt die Werte A, B und a für die beiden Gelatinefraktionen wieder.

Tabelle 6.

Substanz	A	B	$a_{\text{ber.}}$	$a_{\text{beob.}}$
HF I	550	643	94	45
VI	140	164	25	25

Die Werte $a_{\text{beob.}}$ sind identisch mit den a-Werten der Tabelle 5. $a_{\text{ber.}}$ und $a_{\text{beob.}}$ stimmen für VI überein. VI ist also nicht vernetzt und hat Moleküle vom Typ der Fig. 2 a oder 2 b. HF I dagegen ist stark vernetzt, $a_{\text{beob.}}$ ist ja nur halb so gross wie $a_{\text{ber.}}$ Die Moleküle haben im Durchschnitt etwa 50 Ringe.

Es ist nun interessant festzustellen, dass die Fraktion VI in Wasser gelöst und bei Konzentrationen von mehreren Pro-

zent kein Gel zu bilden vermag. Dagegen zeigt HF I in Wasser eine starke Aggregationstendenz und bildet schon in Konzentrationen von 0,25 % ein Gel. Man könnte vermuten, dass die Vernetzung der Gelatinemoleküle eine Voraussetzung für die Gelbildung ist, indem gewisse Teile des Netzmoleküls gegeneinander stärker immobilisiert sind als die offenen Ketten vom Typ der Fig. 2 a oder 2 b. Mit der geringeren Beweglichkeit der Molekülteile kann eine stärkere Absättigung der VAN DER WAALS'schen Kräfte und damit eine starke Aggregation und Gelbildung zusammenhängen. Diese Vermutung muss natürlich durch weitere Untersuchungen geprüft werden.

Zusammenfassung.

1. Die Molekulargewichte von zwei Gelatinefraktionen wurden durch Bestimmung von Sedimentationsgleichgewichten in der Ultrazentrifuge ermittelt. Die eine Fraktion, HF I, die den höchstmolekularen Anteil des Ausgangsmaterials ausmacht, hat ein Molekulargewicht M_w von ca. 89 000, die niedermolekulare Fraktion VI dagegen hat $M_w = 16\,200$. Die früher beschriebenen Verschiedenheiten der Eigenschaften dieser Fraktionen finden also ihre Erklärung in der verschiedenen Molekulargrösse.
2. Die Polydispersität der zwei Substanzen ist verschieden. VI ist durch die Fraktionierung fast einheitlich geworden, während HF I eine ziemlich bedeutende Polydispersität aufweist.
3. Durch Vergleich mit den früher bestimmten Säurebindungsaequivalenten der Fraktionen kommt man zum Resultat, dass HF I aus netzartigen Molekülen bestehen muss, wie sie Fig. 1 symbolisiert, VI dagegen aus einfach gebauten Molekülen vom Typus 2 a oder 2 b.

Herrn Professor THE SVEDBERG möchten wir herzlich danken, dass er es uns ermöglichte, diese Arbeit in seinem Institut auszuführen. Der Rockefeller-Stiftung danken wir für die finanzielle Unterstützung.

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The Constitution and Enzymatic Degradation of Starch and Glycogen.

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The main constituent of starch and glycogen molecules is maltose, the maltose residues being united by 1, 4-α-glucosidic links. In fact, more than 90 per cent of the glucosidic links of starch are 1, 4-α glucosidic in structure. This follows from the fundamental investigations of Haworth and his coworkers on methylated starch (1) and the products of its hydrolysis and from the results of Freudenberg and coworkers (2) for the acid hydrolysis of starch, the optical activity of the products etc.

The end group assay, as worked out chiefly by Haworth and coworkers, shows starch to contain about 4.5 per cent end-groups. This has been confirmed by many investigators. It is possible that starches of different origins have somewhat different end group contents but the differences can only be small. From these results Haworth has concluded that the starch molecule is a simple chain of about 25 glucose residues united by the 1, 4 α glucosidic link (Formula III Fig. 1. In all formulae given in this paper the glucose residue is represented by an arrow, the arrow-head denoting the reducing group and the tail the position 4. Two arrows in the head-tail combination thus indicate maltose, Formula I. The position 6 is represented by the centre of the arrow-shaft. The isomaltose, 6-α-glucosido-glucose, has the formula II).

On the other hand it is quite clear that the particles in a starch solution have a degree of polymerisation (DP) of a much higher order. The ultracentrifugal assay (Lamm (3)) gives values for DP of 1 000—10 000. Furthermore, starch shows pract-

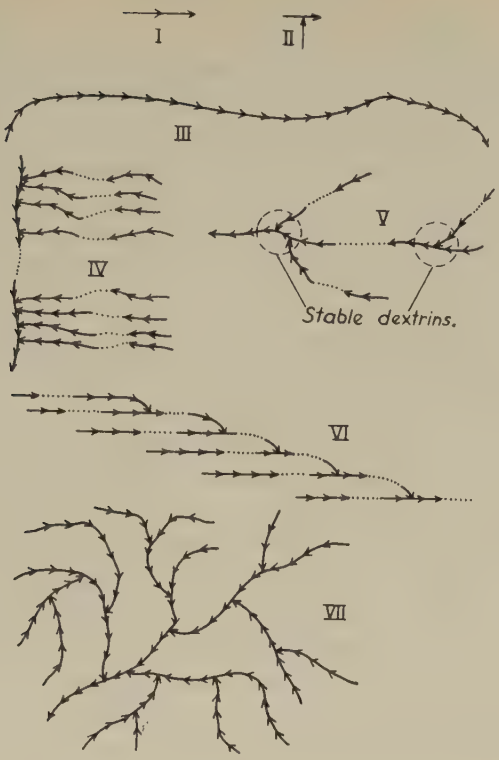

Fig. 1.

ically no reducing properties, so that the content of reducing end-groups must be very small. Ethers and esters of starch show the same high degree of polymerisation as starch itself, and from the esters starch may be regenerated with unaltered molecular weight. From these results STAUDINGER (4) has concluded that the molecules of starch and other polysaccharides are true macro-molecules containing in the case of starch hundreds or thousends of glucose units. The end-group assay, however, gives an average chain-length of only about 25 units, although it must be kept in mind that the calculation of chain-lengths from the end-group values is possible only under the assumption that the chains are simple and unbranched. In order to obtain consistency of the end-group values with the high degree of polymerisation STAUDINGER and HUSEMANN (5) have proposed a branched formulation of starch and

glycogen, later sometimes called the "comb" formulation. These authors assume the molecules to consist of a relatively short "principal chain" with many side chains attached to the principal chain by 1, 6-, 1, 3- and 1, 2-α-glucosidic links (Formula IV). Staudinger and Husemann point out that multiple branching of the chains seems possible.

From investigations of the enzymatic amylolysis, Myrbäck (6) concluded that in starch molecules that are mainly constituted according to the Haworth formula, there exist "anomalies", parts of the molecules that have a constitution different from the simple maltose scheme. Several forms of anomalies were discussed, especially glucosidic links in positions other than the usual 4-position, representing points of ramification. It was assumed that these anomalies are not attacked by the amylases, the presence of the anomalies being the cause of the incomplete saccharification of starch and the formation of the so-called stable dextrins (Formula V). This assumption has proved correct (7) in as much as the stable dextrins of the α-amylases and α-amylase-containing enzyme preparations have been shown to contain anomalous glucosidic links, mainly if not exclusively 1, 6-α-glucosidic links ("isomaltose links").

Haworth, in later papers, has accepted the ramified formulation of starch. Haworth, Hirst and Isherwood (8) in 1937 proposed a "laminated" formulation which Haworth, Kitchen and Peat in a recent paper (9) claim to be the most probable formulation of the starch molecule (Formula VI). This structure is *not* identical with the comb formulation of Staudinger; there is no real principal chain but the reducing group of each chain is attached to, as an average, the central glucose member of the next chain.

Now, if the starch molecule is ramified, the methylated starch must on hydrolysis yield not only tetra- and trimethylglucose but also dimethylglucose and presumably about the same quantity of di- and tetramethylglucose. The various difficulties in isolating the dimethylglucose have been overcome by Freudenberg (10), who regards 2, 3-dimethylglucose as a normal constituent of the products of hydrolysis. Freudenberg therefore accepts a branched formulation of the starch molecule where the side chains have the position 6 on the principal chain.

Obviously under the assumption that the starch molecules are long unbranched chains, HANES (11) has pointed out that 1, 4-α-glucosidic chains of glucose may exist in the form of close spirals, each coil of which contains 6 glucose units. This theory, which has been further elaborated by FREUDENBERG, seems to offer an intelligible explanation of the production of the SCHARDINGER dextrins by *B. macerans* and of the breakdown of starch by the α-maltamylase and other α-amylases. FREUDENBERG has also discussed a formulation of starch in which sidechains are attached in position 6 to a spirally wound principal chain. In a recent paper (12), however, FREUDENBERG has abandoned the idea of a preformed spiral and instead assumes that the macerans-amylase and the α-amylases may arrange parts of the chains in a coil with 6 members or combine with a coil when such occurs.

From experiments on the amylolysis with β-amylase K. H. MEYER (13) has drawn the following conclusions: (I) that the molecule of the true amylose is a simple chain having the HAWORTH formula but containing hundreds of glucose units, (II) that the amylopectin has a strongly ramified structure with multiple branching of the chains. *One* chain has a free reducing group but does not (as for instance in the STAUDINGER formula) play the role of a principal chain. Each chain is attached to another by the 1, 6-α-glucosidic link (Formula VII).

Whereas the non-ramified chains of the amylose are completely broken down to maltose by β-amylase, this enzyme only saccharifies chains with free non-reducing ends of ramified molecules, leaving 50 per cent of the amylopectin as a limit dextrin. This dextrin is sometimes called α-amylodextrin. (In papers from this laboratory we have used the term β-dextrin). MEYER has found that after treatment of this dextrin with a yeast preparation it is attacked again by β-amylase and it is assumed that the yeast enzyme splits off the anomalous end-groups (resulting from the treatment of the amylopectin with β-amylase), whereby normal end-chains are produced from which the β-amylase can release maltose units until its action ceases at the next branching point.

In the theories hitherto briefly outlined no mention is made

of the enzymatic synthesis of starch and the probability of the assumed structures from this point of view. Recently great progress has been achieved in this field and it can be assumed that the synthesis of starch and glycogen starts with glucose-1-phosphoric acid (Cori ester) and is the reverse of phosphorolysis. The synthesis of unbranched chains is then easily understood. In fact the "starch" synthesised seems to consist exclusively of amylose. The synthesis takes place so that a glucose unit in the form of the Cori ester, under liberation of phosphoric acid, is attached in the position 4 to a non-reducing end-group of an existing chain.

Myrbäck and Sillén (14) have attempted to calculate the constitution of amylopectin, glycogen and other ramified molecules from simple working hypotheses on the mechanism of synthesis. In the author's opinion it is very difficult to visualise the enzymatic synthesis of molecules having the formulae proposed by Staudinger, Freudenberg and Haworth and Hirst. When we assume that in amylopectin and glycogen the 1, 6-link is the only one except the normal 1, 4-α-glucosidic link, it must be concluded that in the synthesis of these polysaccharides the attachment of a new glucose unit can occur not only in the position 4 but also to some extent in the position 6. Hence it may be that two different enzymes are in action or that one and the same enzyme has the capacity of attaching a new glucose unit to any free hydroxyl group in the existing chain, the yield of the different glucosidic links formed being determined by steric influences, so that in the case of starch 4.5 per cent and in the case of glycogen 9 per cent of 1, 6-glucosidic links are formed together with the normal 1, 4-links.

It must be assumed that, for instance in a certain plant under certain conditions, the probability of attachment of a new glucose unit in the position 6 (which means ramification of the chain) is in constant ratio with the probability of attachment in the position 4 (which means lengthening of the chain). Assuming that γ is the ratio between these probabilities it is possible to calculate the probable constitution of the molecules formed when synthesis has proceeded for some time. Attachment in the position 4 naturally takes place on end-

groups only. Assuming that the probability of attachment in the position 6 is the same for all free 6-positions, Sillén and Myrbäck have shown that even at moderately low degrees of polymerisation, the degree of ramification, *i. e.* the relative number of branching points, assumes a constant value β. It must be remembered that starches of widely different degrees of polymerisation have nearly the same relative number of end-groups, which must be practically the same as the number of branching points.

In a recent paper Haworth, Kitchen and Peat (9) have attacked the Meyer formulation which they find "needlessly complex and irregular." Haworth, Kitchen and Peat establish that the α-amylodextrin (dextrin-A), which is not attacked by β-amylase, is "sensitised" by a short treatment with salivary amylase or malt α-amylase in the sense that after this treatment it is further attacked by β-amylase under the formation of maltose and a new dextrin-B. This is not sensitised by salivary amylase but is slowly hydrolysed giving fermentable sugar and a new dextrin-C. Haworth, Kitchen and Peat believe that "the mechanism of amylolysis is explicable on the basis of the simple laminated formulation of the structure of starch propounded by Haworth and Hirst, if it be assumed (I) that the impediment to β-amylase action is represented by the polymeric links which unite the unit chains, (II) that the polymeric links are ruptured by an enzymic component of saliva and of malt α-amylase, and (III) that the unit chains so liberated immediately recombine with the formation of new polymeric (*i. e.* 1, 6-α-glucosidic) links with a different orientation of position on the respective chains".

Apart from the fact that the laminated formula bears no relation to a conceivable mechanism of the synthesis, it seems to the present author that the assumptions (II) and (III) are highly improbable and not in accordance with our present knowledge of the action of the α-amylases. (The assumption (I) is generally accepted). A resynthesis of ramified molecules of the assumed kind is in itself improbable, even if it must be admitted that a kind of resynthesis is assumed to occur in the formation of the Schardinger dextrins. The principal objection to the assumptions is, however, that the action of

the α-amylases on the amylodextrin (dextrin-A) does not result in the formation of a substance (dextrin-B) with a *high* degree of polymerisation (which should be nearly the same as that of dextrin-A) as postulated by Haworth. On the contrary, the products of the action of the α-amylases on α-amylodextrin (starch, glycogen) are dextrins (called α-dextrins in communications from this laboratory) of *low* molecular weight, 1 000—4 000, when the first phase of the action ("sensitising") is complete. The sensitising of the dextrin-A described by Haworth, Kitchen and Peat is nothing but the hydrolysis, more or less complete, in which new shorter end-chains are produced, which can be attacked by the β-amylase. That the "sensitising" of dextrin-A is a hydrolysis is clear from the authors' own experiments: dextrin-B reduces Fehling's solution and has a high iodine value; the methylated product has a very low viscosity etc.

The "polymeric links" are not ruptured by the α-amylases in as much as they remain in the stable dextrins (dextrins C and D). The links that are ruptured in this phase of the action of the α-amylases are normal 1, 4-α-glucosidic links, and the reason for their hydrolysis at a very high velocity (as compared with the very low velocity of the subsequent saccharification, phase B → C) is that they are situated at a certain distance from end-groups and anomalies (branching points) (Myrbäck and Sillén (14), (15)). The α-amylases are, as has been pointed out by many investigators, *endo-amylases* capable of attacking any 1, 4-α-glucosidic link of a chain provided that its distance from end-groups and anomalies is not too small (15).

In rejecting the Meyer formulation, Haworth, Kitchen and Peat write: "It is not possible to attach a quantitative significance to the structure proposed by Meyer and indeed it is doubtful if the author intended to express thereby any other than a qualitative interpretation of the facts. . . . On no system of multiple branching of the Meyer type does it seem possible to account for the formation of as much as 50 per cent by weight of dextrin-A." In the present author's opinion it is quite possible to account for the formation of 50 per cent α-amylodextrin from amylopectin or 40 per cent from starch respectively. Myrbäck and Sillén have shown that a

polysaccharide with the end-group content $\beta = 0.045$ (starch), synthesised according to the assumed simple mechanism and quite irregular in structure, will on the action of β-amylase yield 60 per cent of maltose and 40 per cent of dextrin-A. This means that amylopectin ($\beta = 0.056$) will yield 50 per cent. The saccharification of starch and glycogen is quite in accordance with the formulation proposed by Myrbäck and Sillén and it is quite possible to attach a quantitative significance to an irregular structure of the type proposed by us: the molecule may be quantitatively described by stating the degree of ramification, defined as above, the numbers and lengths of chains with free ends and of chains between points of ramification. It is true that these numbers are means, but this is the case also in all other formulations of the starch and glycogen molecules. However, not only can the mean figures for, for instance, the length of chains with free ends be given but it is also possible to calculate the distribution of the glucose units in chains of different lengths etc. It may be mentioned that in starch (amylopectin), the average length of chains between two branching points is calculated as 5—6, which, in the author's opinion is the only fact that justifies the conclusion, arrived at by many investigators (see for instance Hanes (11)), that the units are in some way arranged in groups of six.

The formulation of Myrbäck and Sillén gives a natural explanation of the hitherto not clearly understood action of the α-amylases. The malt α-amylase acts (as the salivary amylase in Haworth's experiments) in two phases. The first (the "sensitising" of Haworth) is the "dextrinogenic" activity (liquefaction) by which the starch molecule is broken up into fragments of fairly low molecular weight; the second (phase B → C in Haworth's experiments) is the "saccharogenic" activity, whereby the α-dextrins (dextrin-B) are more or less completely transformed into maltose. This saccharification is incomplete when the fraction of the α-dextrins used in the experiment contains one or more anomalies, and yields in this case maltose, glucose and stable dextrins, which latter contain the anomalies (isomaltose links). The α-amylases are endo-amylases; they do not, as for instance the β-amylase, require

a free end-group for their attachement to the substrate molecule. On the contrary, glucosidic links in the vicinity of end-groups and anomalies are attacked with a much smaller velocity than links more remote from end-groups and anomalies. Even a simple unbranched chain of 6 glucose units, combined with 1, 4-α-glucosidic links, is only very slowly hydrolysed. Myrbäck and Thorsell have shown (16) that when α-amylase is allowed to act on chains of different lengths (partly hydrolysed starch) the number of glucosidic links that are ruptured with the great velocity characteristic of the liquefaction of starch, is diminished as the chain-length decreases, so that in a substrate with an average degree of polymerisation of about 6 practically no links at all are attacked with the great velocity. We have thus reason to assume that in a chain molecule something like six glucosidic links in the vicinity of the end-groups or anomalies are more or less protected from the attack of the α-amylases (14, 15). On this assumption the action of malt α-amylase on starch is clearly understood. It is a convincing fact, that the hydrolysis by this enzyme of glycogen, which on account of its higher degree of ramification has rather different values of chain-lengths etc. and shows a quite different composition for the primary products of its hydrolysis by α-amylase, may be very well calculated under the same assumptions.

Summary.

Some formulations proposed for the molecules of starch and glycogen are discussed. Most of these formulations bear no relation to any conceivable mechanism of the enzymic synthesis of polysaccharides. From the simplest possible assumptions of the mechanism of synthesis, Myrbäck and Sillén have deduced a formulation with multiple branching of the chains, not unlike the formulation proposed by K. H. Meyer. It is shown that the formulation is in very good agreement with the known facts concerning the enzymic degradation of polysaccharides. It is pointed out that the proposed structure, though irregular and in a sense complicated, may be the object of quantitative calculations and can give a quantitative interpretation to the facts.

In concluding I wish to point out that in my opinion structures of the "irregular" type discussed here are probable also in the case of several other polysaccharides with ramified structure. It is probable that, for instance, the yields of the different methylated glucoses from the methylated polysaccharides can in some cases be calculated just as well from irregular structures as from the regular ones with side chains of fixed length and position etc. which have been preferred hitherto.

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Penicillium notatum als Ausgangsmaterial bei der Darstellung von Vitamin D_2.

Von

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Durch die allbekannten Versuche von Hess und von Steenbock wurde nachgewiesen, dass antirachitisch unwirksame Nahrungsmittel durch Bestrahlung mit ultraviolettem Licht antirachitisch aktiv werden können. Der Chemismus bei dieser Photoaktivierung wurde von Windaus aufgeklärt. Wie aus seinen Arbeiten hervorgeht, können verschiedene Sterine als Provitamine dienen, indem sie durch Bestrahlung in mehr oder weniger stark antirachitisch aktive D-Vitamine umgewandelt werden. So entsteht aus Ergosterin Vitamin D_2 und aus 7-Dehydrocholesterin Vitamin D_3.

Von Bedeutung ist, dass sterinhaltiges Material aus der Tier- oder Pflanzenwelt nach Bestrahlung manchmal eine so erhebliche antirachitische Aktivität erhält, dass es in der Tierzucht als D-Vitaminfutter praktische Verwendung gefunden hat. Bei dem Suchen nach biologischem Material mit einem möglichst hohen Gehalt an photoaktivierbaren Sterinen hat man sich vielleicht besonders den Mikroorganismen zugewandt. Am meisten studiert sind in dieser Beziehung die Hefen. Die gewöhnliche Brauereihefe z. B. erhält durch Ultraviolettbestrahlung eine Aktivität von 300—600 I. E. pro g. Auch Schimmel (*Penicillium sp.*) wurde neuerdings untersucht (1 vgl. auch 2), allerdings mit einem recht bescheidenen Erfolg (140 I. E. pro g Trockensubstanz).

Im folgenden werden wir kurz über unsere bisherigen, diesbezüglichen Versuche mit *Penicillium notatum* berichten. Wie wir gefunden haben, hat nämlich dieser Mikroorganismus einen auffallend hohen Gehalt an Ergosterin und hat nach Bestrahlung eine wesentlich höhere antirachitische Aktivität als sonst in der Literatur in dieser Beziehung beschriebene Mikroorganismen. Wie aus dem biologischen Test mit einerseits Küken und andererseits Ratten als Versuchstieren hervorgeht, ist die antirachitische Aktivität auf den Gehalt an Vitamin D_2 zurückzuführen. Es mag bemerkt werden, dass die Verwendbarkeit von *Penicillium notatum* als D-Vitaminfutter vielleicht ein spezielles Interesse beanspruchen kann, weil die unverhältnismässig hohen Darstellungskosten von Penicillin dadurch zu einem gewissen Umfang kompensiert werden könnten.

Versuche.

Züchtung: Zu den Versuchen wurde ein Stamm von *Penicillium notatum* mit gutem Penicillinbildungsvermögen benutzt. Die Züchtung wurde in Oberflächenkultur auf dem synthetischen Nährboden von Czapek-Dox (3) vorgenommen. Der Nährboden hatte somit folgende Zusammensetzung:

3 g $NaNO_3$ + 1 g KH_2PO_4 + 0,5 g KCl + 0,5 g $MgSO_4 \cdot 7H_2O$ + + 0,01 g $FeSO_4 \cdot 7H_2O$ + 40 g Glucose. Leitungswasser bis 1000 ml.

Der frisch geerntete Schimmel wurde gut ausgepresst, über Nacht bei 85° getrocknet und schliesslich fein gepulvert.

Ergosterinbestimmung (Mitbearbeitet von M. Elander und G. Nilsson): 1 g Trockenpräparat von *Penicillium notatum*, mit 10 ml Wasser + 1 Tropfen Toluol verrührt, wird während 48 Stunden bei 30° autolysiert. Nach Zugabe von 10 g KOH (in Flocken) + 40 ml Wasser wird unter Umschwenken während 1 Stunde auf dem Wasserbade erhitzt. Nach Abkühlen wird im Scheidetrichter 5 mal mit je 50 ml Äther ausgeschüttelt, der Äther verdampft und der Rückstand in warmem Benzol aufgenommen. Von der zweckmässig verdünnten Benzollösung werden 10 ml mit 4 ml Essigsäureanhydrid und dann tropfenweise mit 0,5 ml konz. H_2SO_4 versetzt, wobei die Temperatur

bei etwa 20° gehalten wird. Die auf Zusatz von H_2SO_4 zuerst eintretende Rotfärbung schlägt in intensiv grün über. Die Intensität der Grünfärbung wird genau 4 Minuten nach Zugabe der Schwefelsäure in dem lichtelektrischen Kolorimeter nach Brunius (4) ermittelt. Die Eichkurve wird unter Verwendung von bekannten Mengen reinen Ergosterins konstruiert.

Folgende Tabelle gibt einen Vergleich zwischen einigen von uns in bezug auf sowohl Ergosterin- als auch Gesamtfettgehalt untersuchten Mikroorganismen. Die Fettbestimmungen wurden nach der Methode von Schmid-Bondzynski (5) ausgeführt.

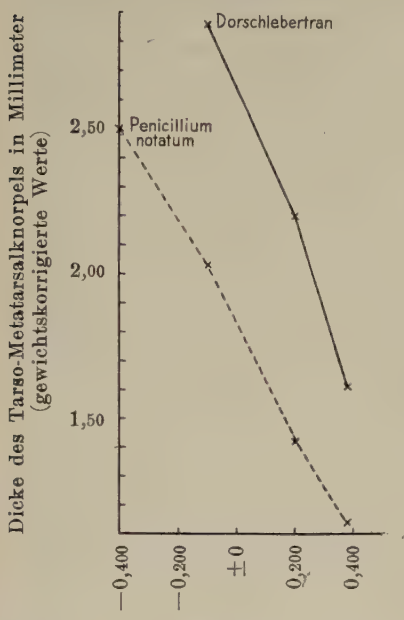
Art	% der Trockensubstanz	
	Fett	Ergosterin
Brauereihefe	5,2	0,31
Torula utilis	7,8	0,26
Penicillium notatum . . .	7,4	0,85
» glaucum . . .	13,1	0,15

Von Interesse ist in dieser Zusammenstellung der Vergleich zwischen *Pen. glaucum* und *Pen. notatum*. Aus dem Fettgehalt eines Mikroorganismus können offensichtlich keine Schlüsse bezüglich dessen Gehalt an Ergosterin gezogen werden. Wie ersichtlich ist der Gehalt an Ergosterin bei *Pen. notatum* beträchtlich höher als bei den sonstigen hier untersuchten Mikroorganismen.

Ultravioletthestrahlung: Der getrocknete und fein zerriebene Schimmel wurde auf einer Aluminiumplatte in einer Schichtdicke von $^1/_3$—$^1/_2$ mm. (entspr. etwa 0,024 g Präparat pro cm^2) unter Verwendung einer Biosollampe (ohne Dorno-Filter) von 250 Watt während 3 Minuten bestrahlt. Der Abstand zum Zentrum des Brenners war 50 cm.

Biologische Wertbestimmung im Kükentest: Die Bestimmung erfolgte nach der von Olsson (6, 7) ausgearbeiteten Methode mit Küken von der Rasse Weisses Leghorn als Testtiere. Als Standard wurde ein Dorschlebertran vom Wirkungsgrad 180 Kükeneinheiten pro g benutzt. (1 Kükeneinheit = der Effekt von 0,01 γ Vitamin D_3 im Kükentest). 3 Gruppen Küken be-

kamen das Standardpräparat und 4 Gruppen das ultraviolettbestrahlte Trockenpräparat von *Penicillium notatum*. In einer Vorperiode bekamen sämtliche Küken ein rachitogenes Futter von folgender Zusammensetzung:



Gemahlener Weizen	36,0 %
» Mais	30,0 »
Sojamehl	13,5 »
Magermilchpulver	10,0 »
Trockenhefe	3,0 »
Luzerneheumehl	6,0 »
Kochsalz	1,0 »
Gepulverte Holzkohle	0,5 »

Dieses Futter enthält 15,8 % schmelzbares Reinprotein, 0,530 % Ca und 0,444 % P. Der Ca/P-Quotient = 1,19 : 1. 7 Tage nach dem Brüten wurde die Vorperiode beendet und die Testperiode angefangen. Während der Testperiode wurde dasselbe Grundfutter benutzt. Nur wurde der Ca- bzw. P-Gehalt auf 1,802 bzw. 1,013 % erhöht, und ferner wurde gemäss der nachstehenden Tabelle D-Vitaminpräparat verabreicht. Die Testperiode dauerte 14 Tage. Die Küken wurden dann als Unterlage für die Wertberechnung gewogen und röntgenphotographiert. Als Mass des Ossifikationsgrads im Kükenskelett wurde die Dicke des Fugenknorpels zwischen den Knochenzonen vom distalen Tarsus und Metatarsus genommen. Diese Grösse wird als tmt bezeichnet. Sämtliche Versuchsdata sind in der folgenden Tabelle zusammengestellt.

Die antirachitische Wirkung der verschiedenen Präparate, geht aus der graphischen Darstellung hervor, welche die Regression vom Rachitisgrad der Küken als Funktion des Logarithmus der zugeführten Menge des Präparats zeigt.

Die ausgeführte Wertbestimmung im Kükentest ergab, dass das ultraviolettbestrahlte Präparat von *Penicillium notatum* eine antirachitische Aktivität besitzt, die 419,4 Kükeneinhei-

Anzahl Küken	g D-Vitaminpräparat pro kg Futter	Mittleres Gewicht der Tiere bei:			tmt-Mittelwert in mm	
		Versuchsbeginn (7 Tage alt)	Versuchsende (21 Tage alt)		Abgelesene Werte	Korrigierte Werte
			Hähne	Hennen		
Dorschlebertran (180 Kükeneinheiten D-Vitamin pro g).						
19	0,8	58	115	97	2,54	2,86
20	1,6	58	123	109	2,02	2,20
20	2,4	58	134	116	1,51	1,61
Penicillium notatum.						
20	0,4	58	109	110	2,24	2,50
20	0,8	58	138	106	1,83	2,03
20	1,6	58	147	126	1,32	1,42
20	2,4	58	144	134	1,10	1,14

ten pro g entspricht. Weil das aktivierbare Provitamin in diesem Präparat, wie es scheint, aus Ergosterin besteht, dürfte die antirachitische Wirkung auf Vitamin D_2 zurückzuführen sein, das sich bei der Ultraviolettbestrahlung aus dem Ergosterin gebildet hat. In internationalen Einheiten ausgedrückt beträgt dann der D_2-Gehalt $419{,}4 \times 12{,}7 = 5\,326$ I. E. pro g. Nach Olsson (7) hat nämlich 1 Kükeneinheit ($= 0{,}01\ \gamma$ Vitamin D_3) bei Küken einen ebenso grossen antirachitischen Effekt wie 12,7 I. E. Vitamin D_2. Unter der Voraussetzung, dass in *Penicillium notatum* das Provitamin ausschliesslich aus Ergosterin besteht, enthält das bestrahlte Trockenpräparat somit rund 5 300 I. E. Vitamin D_2. Es wurde in einer entsprechenden Versuchsreihe festgestellt, dass das unbestrahlte Trockenpräparat von *Penicillium notatum* keine antirachitische Aktivität besitzt.

Die statistische Zuverlässigkeit der biologischen Bestimmung wurde nach Irwin (8) geprüft. Es wurde dabei festgestellt, dass der Vitamingehalt des untersuchten Präparats mit 95 % Wahrscheinlichkeit zwischen 3 569 und 7 950 und mit 99 % Wahrscheinlichkeit zwischen 3 137 und 9 030 I. E. pro g liegt.

Biologische Wertbestimmung im Rattentest: In einer Bestimmung unter Verwendung von 28 Versuchstieren wurde fest-

gestellt, dass das beschriebene Schimmeltrockenpräparat im Rattentest verglichen mit dem ausgeführten Kükentest einen so grossen antirachitischen Effekt hat, dass dadurch die Möglichkeit ausgeschlossen wird, dass es sich hier um Vitamin D_3 handelt. Vielmehr hat das Präparat die volle Vitamin D_2-Aktivität. Weil indessen die Bestimmung als orientierend zu betrachten ist, wollen wir hier auf zahlenmässige Angaben verzichten.

Zusammenfassung.

Es wurde in der vorliegenden Untersuchung gezeigt, dass *Penicillium notatum* einen auffallend hohen Gehalt an Ergosterin besitzt. Ein ultraviolettbestrahltes Trockenpräparat desselben zeigte im Kükentest eine antirachitische Wirkung entsprechend etwa 5 000 I. E. Die hohe Aktivität des Präparats in einem orientierenden Rattentest schliesst die Möglichkeit aus, dass der antirachitische Effekt auf Vitamin D_3 zurückzuführen ist und befestigt die Auffassung, dass das hier vorliegende D-Vitamin aus Vitamin D_2 besteht.

Man dürfte annehmen können, dass die Aktivierung des Schimmeltrockenpräparats durch die vorgenommene Ultraviolettbestrahlung nicht optimal gewesen ist. Versuche, die in anderem Zusammenhang vorgenommen wurden, deuten an, dass durch anders gewählte Bestrahlungsbedingungen eine wesentlich verstärkte Aktivierung zu erreichen ist.

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Fetuin, a New Globulin Isolated from Calf Serum.

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It has long been known that there is some difference between the sera (and plasma) from the new-born animal and that from the adult. In the former case the serum contains less globulin than in the latter. According to earlier investigations by, among others, Howe (1), the proportions between the various globulin fractions are also different in the two instances. It appeared to the present author that some of the serum proteins could perhaps be prepared more easily in a pure condition from calf serum than from that of the cow. The first fractionation experiment carried out on a calf serum immediately showed a distinct difference in precipitability as compared with that for cow serum. An ultracentrifugal investigation of the different globulin fractions revealed the presence in considerable amounts of a new component with $s_{20} \sim 3$ S[1], whereas the normal globulin component with $s_{20} \sim 7$ S only occurred in comparatively small amounts. A number of fractionation experiments have since been carried out on several different calf sera, and the new globulin was found in smaller or greater amounts in all instances. For reasons to be discussed later in this paper, the name fetuin is proposed for this new globulin.

Preparation.

As this new serum protein is present in a relatively larger amount in the calf just after birth it facilitates the prepara-

[1] By unanimous vote at the conference on "The Ultracentrifuge" held by the *New York Academy of Sciences* on November 14—15, 1941, it was agreed that it be proposed that 10^{13} times the fundamental unit for the sedimentation constant (in the C. G. S. system) be called the Svedberg (S).

tion if the serum is obtained from calves not more than 14 days old. Usually their age has been less than one week.

If neutral, saturated ammonium sulphate is added to a mixture consisting of one volume of calf serum and one volume of 0.2 M-NaCl, very little precipitation ordinarily occurs until the salt concentration has reached a value corresponding to 0.37—0.40 Am_2SO_4.[1] From this concentration onwards to about 0.50 Am_2SO_4 most of the fetuin is precipitated together with the other globulins. Within this range more than $^2/_3$ of the fetuin is deposited from 0.36 to 0.42 Am_2SO_4. By dissolving the fractions obtained between these limits and reprecipitating the fetuin at 0.40 Am_2SO_4 the purity of this substance may be somewhat increased. It does not seem possible, however, to remove in this manner a globulin component with s_{20}~20 S.

When the serum is taken from a calf more than a few weeks old it contains considerable amounts of euglobulin (i. e. according to the much used definition of Howe (2), the globulin precipitating between 0.30 and 0.36 Am_2SO_4). In this case it is advantageous to modify the fractionation process somewhat. First, the euglobulin is taken away at 0.37 Am_2SO_4 when the solution must have a pH of between 7 and 8. When the reaction of the filtrate is changed to pH 5.0 by addition of 0.5 N-H_2SO_4, a part of the fetuin will precipitate and is centrifuged down. The reaction of the filtrate is altered to pH 7 and the ammonium sulphate concentration is increased to 0.40. The deposit is rejected since it usually contains but a small amount of fetuin. The pH of the solution is again adjusted to 5.0 and the greater part of the remaining fetuin precipitates. Somewhat more fetuin may be gained by repeating this procedure at 0.45 and 0.50 Am_2SO_4.

If the salting out is carried out at room temperature the fractions obtained at pH 5.0 will often show a definite colour, whereas those from pH 7 are usually colourless. When the fractionation is carried out in the cold room the greater part of the globulins remain colourless or exhibit just a yellow tint. By reprecipitating the fetuin at 0.37 and 0.40 Am_2SO_4,

[1] 0.40 Am_2SO_4 means 40 per cent saturated ammonium sulphate, i. e. 60 volumes solution and 40 volumes saturated ammonium sulphate.

after suitable dilution of the solution, the purity of this protein may be improved. The component with $s_{20} \sim 20$ S which is still present may be considerably reduced by dialysing the fetuin solution against 0.01 M-NaH_2PO_4 after changing its pH to 5. It may also be much lessened by spinning the solution for a sufficiently long time in one of the high-speed centrifuges of the Beams-Bauer type. It seems comparatively easy to obtain fetuin solutions which give rise to a single sym metrical peak in electrophoresis. The mobility corresponds either to that for α_2- or β_1-globulin or lies just between these. It is much more difficult to obtain fetuin solutions which are 100 per cent monodisperse in the centrifuge. The purest solutions so far prepared have contained about 10 per cent of the high molecular component ($s_{20} \sim 20$ S).

Some fractionation experiments still in progress seem to indicate that the following procedure may be useful in the preparation of fetuin. 1 volume of serum is diluted with 1 volume of 0.2 M-NaCl solution and this mixture is precipitated with 3 volumes of neutral, saturated ammonium sulphate solution. The deposit is centrifuged tightly down, resuspended in 1 volume of 0.60 Am_2SO_4 and centrifuged again. After two more washings with 0.60 Am_2SO_4 the precipitate is resuspended in 1 volume of 0.50 Am_2SO_4, left for extraction for an hour or two with occasional stirring and finally centrifuged down. This extraction is repeated at least once and often twice, depending upon the amount of protein in the two first extracts. If its concentration is small in the second extract, a third is omitted. The protein in the extracts is then precipitated by addition of solid Am_2SO_4, centrifuged down and dissolved in water. Finally the two or three solutions obtained from the extracts are united and dialysed against 0.2 M-NaCl. If the same procedure is repeated at 0.45 and 0.40 Am_2SO_4, it is found that the greater part of the fetuin is present just in these two fractions and that it is the predominant component. The 0.45 Am_2SO_4 extract was thus found to consist of 77 per cent fetuin, 23 per cent 7-component, whereas the component with $s_{20} \sim 20$ S was absent. A further fractionation of this extract may result in pure fetuin.

Sedimentation Measurements.

Parallel with the fractionation experiments a number of runs were carried out in the ultracentrifuge in order to follow the variation in the amount of the different components. From these measurements it soon became evident that the sedimentation constant of fetuin varied considerably with the protein

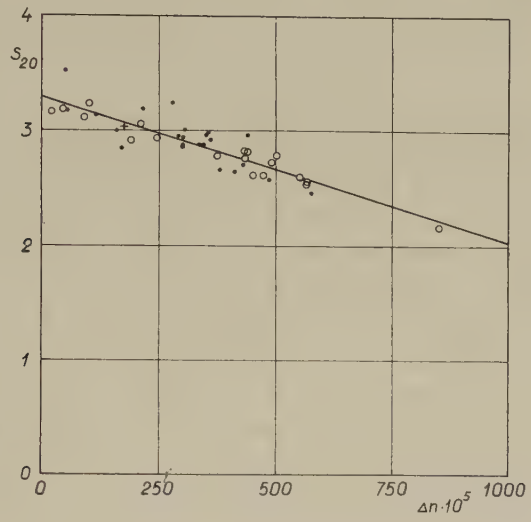

Fig. 1. Variation of s_{20} with concentration of fetuin.

Δn = difference in refractive indices of fetuin solution and of salt solution. • and O values obtained for fractions of calf serum (see text), + value obtained for sheep's foetus.

concentration. In Fig. 1 s_{20} is plotted against the product of the measured Δn for the solution and its relative amount according to the sedimentation diagrams. The points represent values obtained with solutions which were the results of a single fractionation, whereas the circles correspond to those which had been fractionated twice or more. The line has been determined by the method of least squares, where double weight has been placed on the values from the most purified solutions (the circles in Fig. 1). The extrapolated value for zero concentration is $s_{20} = 3.29$ S.

In the sedimentation diagram for diluted calf sera, the presence of fetuin is not revealed by the appearance of a new

peak sedimenting slower than the albumin, but the albumin peak is broader than usual for the same total protein concentration, and sometimes it is definitely asymmetrical, indicating the existance of a more slowly sedimenting component. In undiluted calf serum, however, the fetuin gives rise to a definite peak close to that of the albumin in the sedimentation diagram.

Diffusion Measurements.

The determination of the diffusion constant was carried out at 20.0° C according to the method of Lamm (3). As, however, none of the fetuin solutions so far prepared have been 100 per cent pure, it was necessary to correct for the presence of these impurities. For this purpose a solution was chosen which according to the ultracentrifuge runs consisted of 89 per cent fetuin and 11 per cent of the component with $s_{20} \sim 20$ S. The diffusion curves were averaged by reducing them all to normal co-ordinates, whereby the values for all the individual curves fluctuated slightly about the same curve without showing any drift with time. The curve is shown in the upper part of Fig. 2, where the circles represent the ideal diffusion curve for a homogeneous substance. As the experimental and the ideal curve deviate from each other, the solution contains molecules with different diffusion constants. If we assume that the component with $s_{20} \sim 20$ S has $D_{20} = 1.65 \cdot 10^{-7}$, which is the most likely according to our present experience, we can calculate the theoretical curve for this component at the time when the experimental curve for the mixture is identical with the normal curve. By subtracting this theoretical curve from the normal curve shown in the upper part of Fig. 2 and recalculating the resulting curve to normal co-ordinates the diagram shown in the lower part of Fig. 2 is obtained. The ideal curve is again represented by the circles, but this time the agreement is rather good. From this result we may conclude that the diffusion constant calculated from the resulting curve agrees with that for pure fetuin. The total protein concentration in the experiment was about 0.7 per cent ($\Delta n = 0.00138$). The upper curve in Fig. 2 gave $D_m = 5.08 \cdot 10^{-7}$,

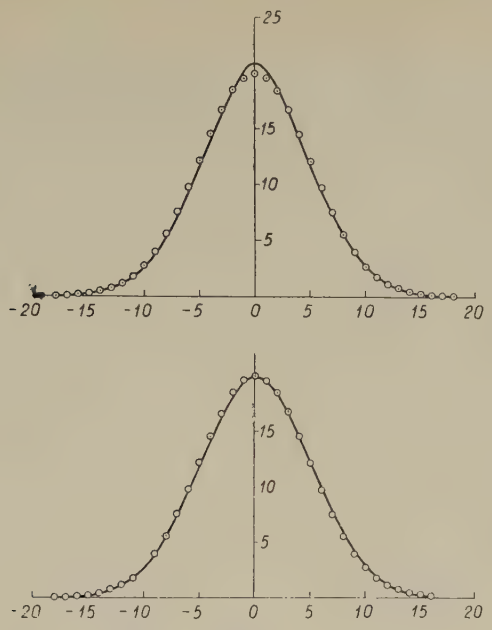

Fig. 2. Diffusion of fetuin.

Upper diagram: Experimental curve recalculated to normal co-ordinates (see text). O ideal curve for a monodisperse substance.

Lower diagram: The same curve after correction for the presence of 11 per cent of the component with $s_{20} \sim 20$ S and reduction to normal co ordinates (see text). O ideal curve for a monodisperse substance.

whereas the corrected lower curve in Fig. 2 gave $D_m = 5.51 \cdot 10^{-7}$ for fetuin. D_m means that the diffusion constant is calculated according to the "moment" method (cf. GRALÉN (4)).

Molecular Weight and Frictional Ratio.

According to the formula of SVEDBERG (5)

$$M = \frac{RTs}{D \cdot (1 - \overline{V}\varrho)}$$

we find $M = 51\,000$ from $s_{20} = 3.29$ S, $D_{20} = 5.5 \cdot 10^{-7}$ and $\overline{V} = 0.714$.[1] From equation 70 b in (6) we have $f/f_0 = 1.59$, which is a comparatively high value for such a low molecular protein.

[1] The author is indebted to Professor CARL DRUCKER for making this determination.

If it be assumed that the particle is unhydrated and that it behaves hydrodynamically like a rotational ellipsoid, $f/f_0 = 1.59$ corresponds to an axial ratio of one to eleven.

If fetuin belongs to the SVEDBERG multiple system, which has mainly been based upon the molecular weights found for the respiratory proteins, it must be placed in the 3-multiple group ($3 \cdot 17\,600 = 52\,800$) as the first member found in this group.

Discussion and Conclusions.

By an ultracentrifugal investigation of the fractionation of calf serum it was found that a new protein was precipitated between about 0.36 and 0.45 Am_2SO_4. This globulin showed properties in the ultracentrifuge entirely different from those of any other serum protein yet investigated. In the sera from young calves it amounted to as much as about 20 per cent of the total protein, and the globulin fraction of the sera contained from 50 to 80 per cent of this new substance. In the serum from a six months old calf, however, the corresponding values were reduced to 5 per cent of the total protein and about 20 per cent of the globulin. In fractions from adult cow serum the presence may be demonstrated of a substance with the same ultracentrifugal properties as fetuin, but the amount of this substance is only a small part of that found in the corresponding fractions from the serum of the six months old calf.

The concentration of the fetuin in the calf blood thus seems to be greatest at birth, then successively decreasing and finally attaining a very low level in the adult animal. It therefore seems reasonable to assume that the fetuin concentration shows its maximum value in the foetus and that it is in some way associated with the period when the greatest building and development of the animal takes place. The author therefore proposes that this new protein be called fetuin. The name is derived from the Latin name for foetus, viz. *fetus*.

It may be objected that it is not sure that the fetuin is present in the serum of the foetus, but that it could appear in the serum after the birth, for instance after the new-born animal has received the colostrum. According to HOWE (1) there

is a strong increase in the globulin fraction of serum shortly after the calf has been suckled for the first time. That a substance like fetuin is present in foetal serum seems very likely from an unpublished ultracentrifugal investigation carried out by M. E. Adair, G. S. Adair and the author. In this study, which was started on the initiative of the Drs. Adair, but was discontinued by the outbreak of the war, it was found that no measurable amount of globulin with $s_{20} \sim 7$ S could be demonstrated in 85 to 134 days old foetus from sheep, whereas the sedimentation diagram for serum from a 24 hours and a 14 days old lamb showed the presence of large amounts of the component with $s_{20} \sim 7$ S. The "albumin peak" from foetal serum, however, was of a composite nature and showed the presence of considerable amounts of another component which the author must now interpret as fetuin. In the diagrams for the 24 hours old lamb the "albumin peak" was still asymmetrical, but in the case of the 14 days old lamb this peak appeared almost symmetrical. In order to verify the presence of the fetuin in sheep's foetus, 5 ml of serum[1] from a 128 days old foetus was fractionated in the same manner as used for preparing fetuin from calf serum. The fraction which was expected to contain the greater part of the fetuin was then run in the centrifuge and showed a single almost symmetrical peak with $s_{20} = 3.03$ S ($\Delta n = 0.00178$). The value found for the sedimentation constant agrees completely with those found for fetuin from calf (see Fig. 1).

According to a private communication, Svedberg and Andersson found several years ago that no component with $s_{20} \sim 7$ S was present in serum from chicken embryo after 11 or 15 days incubation. The "albumin peak" in the sedimentation diagram, however, was very asymmetrical and gave comparatively low values for the sedimentation constant. After 18 days incubation the globulin amounted to 22 per cent of the protein and the "albumin peak" had become more symmetrical. In the serum from a one day old chicken the appearance was much the same.

From what has been said above it seems reasonable to assume

[1] The serum had been kept at −15° C in Cambridge for about one year and then at −8° C for five years in Uppsala. It appeared completely fresh.

that fetuin is often present in considerable amounts in foetus serum but decreases after birth as the young animal grows.

During the last year some publications have appeared dealing with the electrophoresis of serum from new-born and young animals. They all show the presence of large amounts of α-globulin, small amounts of β-globulin and the absence of γ-globulin in the sera of the new-born calf (7, 8) and the new-born foal (9).

The isoelectric point of the α-globulin was found by Clemente and Huddleson (8) to be at pH 4.98, in good agreement with the author's finding that fetuin does not show any measurable mobility at pH 5.0.

The study of fetuin is being continued.

[Note added June 1st, 1944.]

In some recent experiments with serum from cow's foetus (8—9 months) the sedimentation diagram showed the presence of a component with a sedimentation constant equal to that of fetuin. Fractionation experiments carried out in a similar way as described above gave globulin fractions the main part of which were pure fetuin. The globulin with $s_{20} \sim 7$ S could just be demonstrated in the fractions precipitated at pH 5, whereas the component with $s_{20} \sim 20$ S amounted to 6—8 per cent in the same fractions. The amount of fetuin in this foetal serum was 34 per cent of the protein. 88 per cent of the globulin fraction consisted of fetuin, the globulin component with $s_{20} \sim 7$ S making only 4 per cent and the remainder being the high molecular globulin. From these experiments it would seem preferable to prepare the fetuin from foetal serum.

Summary.

1. A new globulin has first been isolated from calf serum. In new-born calves it amounted to about 20 per cent of the total serum protein but to 50—80 per cent of the globulin fraction. In a six months old calf the corresponding values were 5 per cent of the total protein and 20 per cent of the globulin. Later experiments have shown that in serum from cow's foetus the new globulin may amount to as much

as one third of the total protein and about 90 per cent of the globulin fraction. — It has been proposed that this new protein be called fetuin.

2. The sedimentation constant of fetuin varies considerably with its concentration. The extrapolated value for $c = 0$ is $s_{20} = 3.29$ S. The diffusion constant is $D_{20} = 5.5 \cdot 10^{-7}$.
3. The molecular weight of fetuin is 51 000, as calculated from the sedimentation and diffusion constants. The molecule deviates considerably from the compact spherical shape and has $f/f_0 = 1.59$. Its hydrodynamical behaviour is equal to that of an oblong rotational ellipsoid with an axial ratio of 1 : 11.
4. A substance with properties similar to those of fetuin has been found in the serum from sheep's foetus. The possibility of the fetuin being an ordinary component of foetal blood has been mentioned.

The expenses connected with this study have been defrayed by grants from the Nobel Fund and the Rockefeller Foundation.

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Manuscript received May 9th, 1944.

Cytoplasmic Structure of the Sea Urchin and Starfish Egg.

By John Runnström and Ludwik Monné.

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Microscopical examination of the cytoplasm of the sea urchin egg reveals that its ground-substance is not homogeneous[1] (cf. Fig. 1). Its structure seems to justify the old distinction between spongioplasm and enchylema. For the literature, Wilson (1) should be consulted. The spongioplasm forms a continuous microscopic lattice which is more gelated than the enchylema, the fluid substance which fills the interspaces of the lattice. Especially in the egg of *Echinocardium cordatum*, granules were observed to exhibit Brownian movement within the enchylema (2).

The continuous substance of the spongioplasm is not uniformly distributed. It contains numerous grain-like nodes. The diameter of these is somewhat below 1 μ. On stretching, the spongioplasmic nodes assume a more pronounced spindle shape. From observations on centrifuged eggs it is evident that the mitochondria and the yolk granules do not adhere to the spongioplasmic lattice. The Golgi apparatus, on the other hand, is always located in the centrifuged eggs of *Psammechinus miliaris* in the region where the spongioplasm is highly condensed.

The two components of the cytoplasmic ground-substance

[1] When nothing is stated to the contrary, the descriptions refer to the mature, unfertilized or to the fertilized, not yet segmented egg. The following species have been used: *Psammechinus miliaris, Echinocardium cordatum, Strongylocentrotus droebachiensis, Echinus esculentus,* and *Asterias rubens.*

may be gradually separated, as was recently described by Monné (3); cf. also Runnström (2). This is brought about by immersing specimens of the littorial form (*Z*-form) of *Psammechinus miliaris* in sea water of higher salinity (about 32 pro mille) than that to which the animals are accustomed in their natural habitat (about 25 pro mille). The central parts of the mature eggs of females subjected to the hypertonic medium become rich in enchylema, whereas the spongioplasmic lattice is concentrated to the peripheral part of the egg. The mitochondrial granules are squeezed out from the condensed spongioplasm and are found on the border between the peripheral spogioplasmic and the central enchylematic region (cf. Fig. 2). In this same border region coarser fibrils are also often observed which evidently arise by fusion of the slender elements of the normal lattice. These fibrils present a birefringence which is negative with respect to their longitudinal axis.

Fig. 1. Diagrammatic representation of the spongioplasmic lattice of the sea urchin egg.

It is evident from these observations that a more or less complete separation may occur under certain conditions between the spongioplasmic and the enchylematic components of the ground-cytoplasm. It has often been observed that hyaline globules form on the surface of eggs exposed to sea water of pH 3—4. The obvious explanation of this phenomenon is that the continuous lattice of the spongioplasm contracts when exposed to the acid medium. Enchylematic substance is then squeezed out in the form of droplets from the surface of the egg.

In the normal egg, a double refraction is observed in the cortical layer. The birefringence is positive with respect to the radial direction. The value of the retardation (Γ) was determined by means of the rotating mica comparator; it amounted on the average to 9.5 mμ, no perceptible difference being found between the fully grown ovocyte, the mature unfertilized or fertilized eggs. The birefringence of the cortical

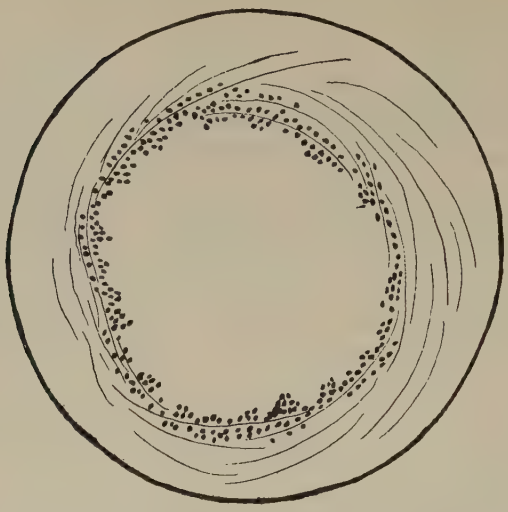

Fig. 2. Egg from a female subjected to a hypertonic medium. The granules mark the border region. Within and around this birefringent fibrils are visible.

layer disappears or is highly reduced by subjecting the eggs to the action of lipid-dissolving agents. Thus it seems probable that the birefringence is due, as in the myelin sheath of nerves, to oriented lipid layers separated by protein films. This assumption also agrees well with the optical properties observed. There are no means of directly ascertaining the thickness d of the birefringent layers, but a rough estimation based on the value found by Schmitt and Bear (4) for the double refraction $(n_a - n_0)$ of lecithin gives an order of magnitude for d of 1 μ (as is well known, $\Gamma = d(n_a - n_0)$).

In the cortical layer, the microscopic spongioplasmic lattice is more ordered than in the parts remoted from the egg surface. In the cortex, the spongioplasmic nodes are somewhat elongated in a direction parallel to the surface. It seems probable that the birefringence is due to the spongioplasmic elements which, near the surface, are oriented in a few parallel layers.

Similar conditions to those prevailing in the cortex are observed in the ovocyte around the large nucleus. Here also an ordered spongioplasmic layer presents a birefringence which is positive with respect to the radius. Evidently, a spontaneous

orientation of the spongioplasm occurs along the external or internal surfaces.

When eggs of the starfish *Asterias rubens* are immersed in a mixture of about one part sea water and three parts pure glycerine, a strong shrinkage of the egg ensues. The whole egg now appears birefringent. When the gypsum plate R I is introduced, the egg appears as a beautiful mosaic of blue and yellow regions. In the *Asterias* egg, it could be clearly established that the birefringence resides in the spongioplasmic lattice and that the sign of the birefringence is negative with respect to the longitudinal direction of the spongioplasmic

Fig. 3. Diagrammatic representation of a *Psammechinus* egg immersed in glycerine and observed between crossed nicols. The arrow marks the direction of lower optical elasticity of the gypsum plate. R I. The dark field is in reality blue, the light one yellow. In the middle the pit.

threads. In consequence of the great volume decrease, most of the spongiplasmic elements are ordered and their intrinsic birefringence is manifested. It has already been mentioned that in eggs from females subjected to a hypertonic medium, fibrillar elements, formed by fusion of the normal elements, present a birefringence. For older data about a more general birefringence of the cytoplasm, the reader is referred to Runnström (2) and Schmidt (5). Eggs of *Psammechinus miliaris S* were also exposed to glycerine. These eggs very often shrank in a characteristic way. A deep pit was formed from the egg surface, the rest of this latter remaining smooth. The whole egg now appeared as a positive spherite (cf. Fig. 3). The spongioplasmic lattice had evidently become ordered into concentric rings parallel to the border of the pit. Gradually, the glycerine penetrated into the egg and a swelling and disappearance of the birefringence resulted. The swelling was great, especially in a layer below the cortex (cf. Fig. 4). Here slender threads extended between the thin cortex and the inner

granular bulk of cytoplasm. The swollen vacuolated layer was lacking below the pit which even after the penetration of glycerine was still visible.

The jelly of the sea urchin egg was precipitated by a solution of a protamine (6, 7) (for example, a 0.1 per cent solution of salmin sulphate). The jelly is in its normal state invisible, because its refractive index is very close to that of water. The jelly has the character of a mucin (6). On addition of salmin,

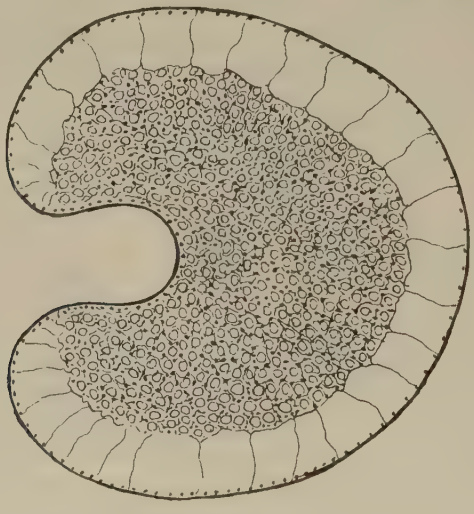

Fig. 4. *Psammechinus* egg with the peripheral part swollen as a consequence of penetration of glycerine. To the left the pit.

the jelly precipitates; at first, a well defined outline appears and, then, gradually the jelly contracts. The precipitated jelly presents a birefringence which is negative in the radial direction – the sign is consequently opposite to that found in the cortical layer of the egg. This is due to the absence of oriented lipids in the precipitated jelly. The birefringence of the jelly disappears when it is immersed in glycerine. Thus, we have to deal in the jelly with a birefringence of form. It is of interest to observe that, when the jelly contracts, a microscopic structure appears in the jelly substance which very much recalls the texture of the cytoplasm. Rows of granules appear which seem to be connected by finer strands. These strands on the whole run parallel to the surface.

There are certain similarities between the phenomena briefly described above and the results obtained with plant viruses by Bernal and Fankuchen (8). The seperation of the cytoplasm into two layers in the eggs from the females brought into a hypertonic medium recalls the separation of the virus preparation into two phases, one disordered and one ordered (top and bottom layers). Furthermore, Bernal and Fankuchen describe the extrusion of a layer of impurities on the settling of the bottom layer. This corresponds in our case to the extrusion of the mitochondrial granules from the peripheral part of the hypertonicity eggs (Fig. 2).

Just as the gels formed by the virus preparations, the spongioplasm may be described as a "liquid crystalline branched aggregate". It is even tempting to regard the spongioplasm as consisting of fused tactoids, the form of the spongioplasmic framework giving a certain support to such a view.

We are not so well informed about the submicroscopic structure of the spongioplasm as about that of the virus preparation. The structure of the spongioplasm is an ordered one, or it may easily become ordered on extraction of water. Evidently, the water content of the spongioplasm may vary like that of the virus gels. pH and electrolyte content are in both cases determining factors. In sea urchin eggs, lack of potassium evidently causes a contraction and concentration of the spogioplasm to the peripheral part of the cell (9). Presumably the water content of the spongioplasm may vary in different parts of the egg, during different stages of cell division, and during different stages of development. At fertilization, a very transitory mild contraction occurs, beginning at the point of entrance of the sperm (for literature, cf. (10)). Some factor may temporarily be at play which causes a decrease in the water content of the spongioplasm (acid formation (11), Ca release (12)). Under abnormal conditions, the contraction following the fertilization may be more pronounced and last for a longer period (e. g. 15—20 minutes).

A fascinating problem is the relation between the cytoplasmic structure and the determination of the different parts of the egg with respect to their fate during the development. It is well known that no fixed determination prevails in the

sea urchin egg. (cf., for literature, Hörstadius (13) and Lindahl (14)). A certain polarity exists which corresponds to the future anterior-posterior axis of the larva. Furthermore, a certain labile dorsiventral organisation probably exists in the egg. In the unfertilized egg of the sea urchin *Echinocardium cordatum*, the animal pole is marked by a papilla. It can be readily observed that the spongioplasmic arrangement differs in this point from other parts of the cortex. It constitutes a weak region which on application of pressure to the egg will burst and let the interior cytoplasm extrude. Förster and Örström (15) observed the formation of a deep pit on the surface of unsegmented eggs of *Paracentrotus lividus* exposed to a KCN solution in sea water. Moreover, they were able to show that the deep pit corresponds to the future ventral part of the embryo. Some differences in water binding capacity may exist between the future ventral and other parts of the egg. With respect to this, the formation of a pit in the eggs of *Psammechinus miliaris* immersed in glycerine may be of interest. It remains to be seen whether this case has any bearing on the determination of the egg.

All the work on living material has been carried out at Kristineberg, the Zoological Station of the Swedish Academy of Sciences. We are very indebted to the staff of the station for their ready helpfulness.

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On the Molecular Weight of Gum Arabic.

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O'Sullivan's (1) pioneer investigations on the constitution of plant gums revealed the fundamental fact that they are all built up of a complex acid nucleus to which is attached readily hydrolysable sugar units. Later investigations (2) have shown that the acidic properties are due to the presence of uronic acid units and that the gums thus may be included in the class of complex polysaccharides termed polyuronides, along with pectic substances, alginic acid etc. In recent years Smith (3) has given, in a series of papers, a detailed account of his investigations of the constitution of gum arabic and "notwithstanding the difficult and complicated nature of the problem, so much progress has been made that the main features of the structure of the repeating unit have been elucidated and the possibilities remaining in structural detail have been very considerably narrowed down", to quote Hirst (4). On the basis of these researches, a possible arrangement of the constituents in the repeating unit of the molecule has been pictured (Fig. 1).

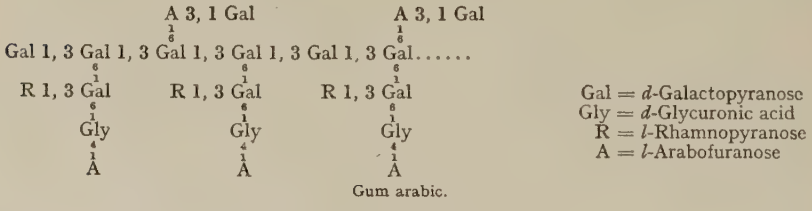


Fig. 1. Possible arrangement of the constituents in the repeating unit of the gum arabic molecule. (Hirst, 4).

On hydrolysis with dilute acids or even autohydrolysis the pentose units are easily split off and a degraded gum is left.

While considerable progress has thus been made as to the constitution and the structure of gum arabic, little is known about its average particle or molecular weight and the distribution of the particle sizes. As a matter of fact the present author has found only one paper dealing with determinations of the molecular weight of this substance. In connection with the description of a new type of osmometer for measuring low osmotic pressures, Oakly (5) gives data from experiments on gum arabic. The smallest measurable pressure was found to be about 5 mm of water at a gum concentration of about 0.5 per cent. The pretreatment of the substance and the composition of the electrolyte solution used as a solvent proved to be of great influence upon the osmotic pressure. Thus electrodialysed gum in 0.02 N-HCl had an osmotic pressure corresponding to a molecular weight of 285 000 at infinite dilution, while after neutralization the pressure in 0.1 N-NaCl was equivalent to a molecular weight of about 250 000. Non-electrodialysed sodium gum, which had been prepared by dialysis of acid gum against 0.1 N-NaCl at 0° C for three weeks, had apparent molecular weights varying from 152 000 to 175 000 as the concentration of sodium chloride in the solvent varied from 0.11 N to 0.96 N. Calcium gum prepared in the same way as the sodium gum had an osmotic pressure in 0.084 N-$CaCl_2$ corresponding to a molecular weight of 225 000. These large discrepancies in the apparent molecular weight of either of the two samples may be accounted for in two different ways, according to Oakly. Either one may assume an aggregation of the gum particles varying under the different experimental conditions or else the variations may be ascribed to varying degrees of suppression of the ionic pressure difference due to Donnan equilibrium. Oakly seems to be of the opinion that the latter interpretation is the correct one.

* * *

The gum dealt with in the present investigation was an acacia gum of high quality. The substance was purified by acidifying a 20 per cent aqueous solution with hydrochloric

acid and precipitating the gum in three volumes of alcohol. After three such precipitations the gum was dissolved in water and the solution dialysed against distilled water until the chloride ions had disappeared, i. e. after about one or two days with frequent changes of water. The ash content was thus easily diminished from about 3 per cent to about 0.05 per cent.

For purposes of comparison some data frequently reported in papers on gums are given below.

1. *Optical rotation.*

$$[\alpha]_D^{20^\circ} = -28 \ (c = 2.7 \text{ per cent}).$$

Thomas and Murray (6) reported $[\alpha]_D^{25^\circ} = -24.3$ ($c = 1$ per cent) for Sudan gum and Smith (7) $[\alpha]_D^{20^\circ} = -28$ ($c = 2$ per cent) for the gum used in his investigations.

2. *Equivalent weight.*

   a. From the sodium content of the sodium salt, according to Bungenberg de Jong and van der Linde (8): 1 318 and 1 308.

   b. From titrations at room temperature (bromthymol blue): 1 314 and 1 309.

   c. From titrations after heating the mixture of solution and standard alkali at 100° C for half an hour: 982 and 997.

   d. From the content of carboxyl groups determined according to Lefèvre and Tollens (9): 995 and 983.

Values varying from 1 000 to 1 400 have been reported in the literature. It seems probable from the figures given that some of the carboxyl groups are occupied under ordinary conditions in lactone formation. Cf. Butler and Cretcher (2).

3. *Glucuronic acid anhydride* according to the method of Lefèvre and Tollens (loc. cit.): 17.7 and 17.9 per cent.

4. Acidity and viscosity.

Table 1. Electrodialysed Gum at 20° C.

Concentration, per cent	pH	η/η_{H_2O}
3.16	2.44	2.423
1.58	2.67	1.825
0.79	3.90	1.506
0.40	3.16	1.311
0.20	3.46	1.189
0.10	3.75	1.118
0.05	4.10	1.061

* * *

The mean molecular weight of the gum was determined in two different ways, viz. from measurements of sedimentation in the centrifugal field and diffusion on the one hand, and from sedimentation equilibrium on the other (10, 11). In the first case the molecular weight is calculated by means of the formula

$$M = \frac{R\,T\,s}{D\,(1 - V\varrho)}, \qquad (1)$$

where R = gas constant, T = absolute temperature, s = sedimentation constant, D = diffusion constant, V = partial specific volume of the substance studied and ϱ the density of the solvent.

From sedimentation equilibrium the molecular weight is calculated by means of the formula

$$M = \frac{2\,R\,T \cdot \log\,(c_2/c_1)}{(1 - V\varrho) \cdot \omega^2\,(x_2^2 - x_1^2)}, \qquad (2)$$

where c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the centre of rotation and ω is the angular velocity of the centrifuge rotor.

Sedimentation.

A series of typical sedimentation curves is shown in Fig. 2. At a given time there is only one maximum in the sedimentation diagram. As it is very probable that the gum contains particles of different sizes, the sedimentation constant calculated from such diagrams may be taken as an average, the definition of which may be left an open question for the present.

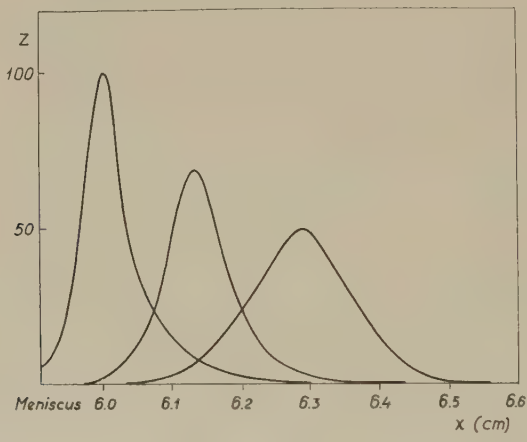


Fig. 2. Sedimentation diagram from the run with a 0.5 per cent solution of gum arabic. Medium: 0.2 N-NaCl. Abscissae: Distance from centre of rotation. Ordinates: A quantity, Z, proportional to the concentration gradient dc/dx. The maximum ordinate of the curves marks the mean position of the boundary between solvent and solution after the sedimentation has been proceeding for 10, 30 and 60 minutes. Centrifugal force: 100 000 times gravity.

The variation of the sedimentation constant with different factors is shown in Tables 2 and 3 and Fig. 3. The sedimentation constant is given in Svedberg units, S; one $S = 10^{-13}$ cm/sec. dyne.

Table 2. Variation of s_{20} with Concentration of NaCl. Concentration of gum: 0.5 per cent.

Normality, NaCl	0.000	0.001	0.005	0.025	0.100	0.200
s_{20}	2.7	5.5	7.1	8.4	8.9	9.0

The very marked dependence of s upon salt concentration is due to charge effects, the theoretical interpretation of which

has not yet been satisfactorily established (cf. the diffusion anomalies mentioned below). From the table and Fig. 3 a, it is seen that 0.2 N-NaCl will suffice to eliminate the charge effects at least for concentrations of gum up to 0.5 per cent and in reality it will do so even for higher concentrations.

Table 3. Variation of s_{20} with Concentration of Gum.

Concentration of gum, per cent	Acid gum			Sodium gum
	Medium			Medium
	0.2 N-NaCl	0.2 N-$CaCl_2$	0.2 N-$La(NO_3)_3$	0.2 N-NaCl
1.00	8.3	—	—	7.7
0.75	8.5	8.6	8.8	8.2
0.50	9.1	9.4	9.4	8.9
0.25	10.0	9.9	10.1	9.5
0.10	10.3	—	—	10.2

From Table 3 it is seen that there are only slight differences between the values of the sedimentation constants for acid gum and sodium gum in 0.2 N-NaCl. The dependence of the sedimentation constant upon concentration seems to be linear (Fig. 3 b). On extrapolation of s to zero concentration, the value $s_{20} = 10.7$ is obtained for acid gum and $s_{20} = 10.4$ for sodium gum. The sodium gum was prepared by neutralizing *electro-dialysed* gum with 0.10 N-NaOH. The large differences between electro-dialysed and non-electrodialysed gum found by Oakly in his osmotic pressure measurements thus do not correspond to equally marked differences in sedimentation. The influence of the prolonged dialysis (three weeks) against 0.10 N-NaCl may possibly have been overlooked by Oakly.

The exchange of NaCl for $CaCl_2$ or $La(NO_3)_3$ of the same equivalent concentration brings about a slight increase of the sedimentation constant at higher concentrations of gum. On extrapolation, however, the constant appears to attain the same value as that obtained for acid gum in 0.2 N-NaCl.

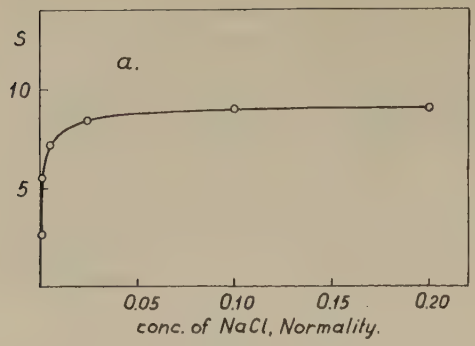
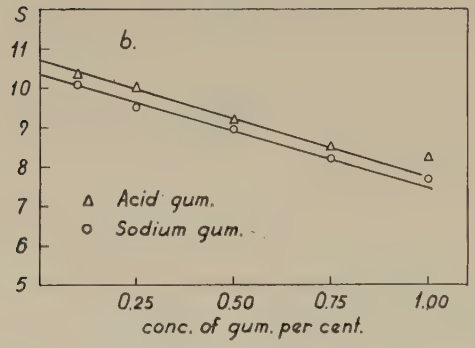


Fig. 3. *a*. Dependence of the sedimentation constant upon salt concentration for a 0.5 per cent aqueous solution of gum.



b. Dependence of the sedimentation constant upon concentration of gum. Medium: 0.2 N-NaCl.

Diffusion.

Diffusion experiments were performed according to the method worked out by Lamm (11). The diffusion constants were calculated from diffusion curves the appearance of which is shown in Fig. 4. The properties of these curves permit the calculation of the diffusion constant from a variety of formulae. Taking the moments about the ordinate axis we get the constant D_m and from the area and the height (maximum ordinate) of the curve we obtein D_A. An ideal diffusion curve would of course give $D_m = D_A$. — The diffusion constants are given in units of 10^{-7} cm^2/sec.

From Table 4 it is seen that there are slight differences between the D_m and D_A values throughout the measurements. This fact is probably due mainly to the polydispersity of the substance. The diffusion of acid gum seems to proceed at the same velocity in 0.2 N-NaCl as in 0.2 N-$CaCl_2$. The diffusion

Table 4. Diffusion of Gum Arabic. Temperature: 20° C.

Diffusion time, hours	Acid gum in 0.2 N-NaCl						Acid gum in 0.2 N-$CaCl_2$		Sodium gum in 0.2 N-NaCl	
	$c = 1$ %		$c = 0.5$ %		$c = 0.25$ %		$c = 0.5$ %		$c = 0.5$ %	
	D_m	D_A	D_m	D_A	D_m	D_A	D_m	D_A	D_m	D_A
26	—	—	—	—	2.3	1.9	2.4	2.2	—	—
33	—	—	3.0	2.5	—	—	—	—	—	—
42	—	—	—	—	2.4	2.1	2.6	2.3	2.7	2.5
48	2.5	2.0	2.4	2.2	2.3	2.2	2.3	2.1	2.8	2.5
57	2.3	2.1	2.3	2.1	2.3	2.1	—	—	—	—
66	2.4	2.1	—	—	2.4	1.9	—	—	2.5	2.4
72	2.4	2.1	2.2	2.2	—	—	—	—	—	—
81	2.5	2.1	1.9	1.9	—	—	—	—	—	—

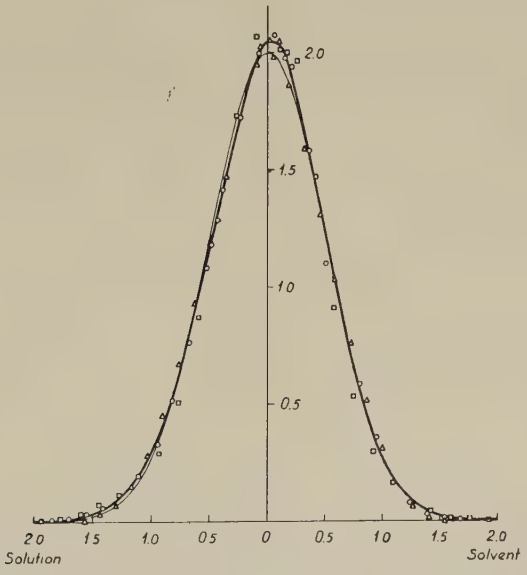


Fig. 4. Diffusion of acid gum in 0.2 N-NaCl. Concentration: 0.5 per cent. Circles, squares and triangles represent experimentally determined coordinates, obtained from exposures taken 33, 57 and 81 hours after the beginning of the diffusion process. The faintly drawn curve is the normal ideal curve.

constant of sodium gum is slightly higher than that of the acid substance. In the concentration interval investigated, no clear variation of the diffusion constant with concentration can be established.

The co-ordinates determining the experimental diffusion curves may be converted into so-called normal co-ordinates (cf. Lamm, *loc. cit.*) from which the normal curve is drawn. If the normal *ideal* curve is also drawn we have an opportunity of estimating the degree of deviation from ideal diffusion in the actual case. As seen from Fig. 4 the normal curve for gum exhibits only a rather small deviation from the ideal curve.

It should also be mentioned that the diffusion of either acid or sodium gum in pure water is quite anomalous owing to the charges of the particles and the diffusion potential set up by the ions on account of their different mobilities. The diffussion curves obtained are strongly asymmetrical, permitting only rough estimations of the diffusion constants. Values of the magnitude $40 \cdot 10^{-7}$ cm^2/sec., i. e. about twenty times the normal values, are obtained. The theoretical interpretation of these anomalies has been discussed by Bruins (12) and by Hartley and Robinson (13) among others.

Partial Specific Volume.

The partial specific volume was determined pyknometrically. The pyknometer used had a volume of about 55 ml. The value of the partial specific volume, V, was calculated according to the formula

$$V = v\left(1 - \frac{100 - p}{m} \cdot \frac{dm}{dp}\right),$$

where v = specific volume of the solution,
m = weight of the pyknometer content,
p = concentration of the substance in weight per cent.

The function $m = f(p)$ was found to be strictly linear within the concentration range investigated (up to 5 per cent) and dm/dp thus constant for a certain medium. The values of V in some different media are given in Table 5.

Table 5. The Partial Specific Volume of Gum Arabic at 20° C.

Medium	pH	conc., per cent	
		0.5	zero
Sörensen's phosphate buffer	6.84	0.623	0.621
Mc Ilvaines buffer	3.90	0.619	0.618
Do.	2.28	0.612	0.611
0.2 M-NaCl	2.79 [1]	0.614	0.612

The measurements of V have been performed with such precision as to give significance to the third decimal. All values may be impaired by a systematic error of about ± 0.2 per cent owing to a possible error of about ± 0.3 per cent in the concentration value of the stock solution. As seen from the table the partial specific volume of the gum is dependent upon the acidity of the solution. Such a dependence was found also for other polyuronides. The specific volume of some pectic substances, for instance, may vary by about five per cent according as the solution of the substance is neutral or acid. It may be left an open question whether this variation is real or only apparent, caused by solvent density variations due to alterations in the hydration of the particles.

Mean Molecular Weight.

The data necessary for calculating the molecular weight from formula (1), p. 511, are summarised below. The values of s and D are reduced to water of 20° C, hence the density of the solvent is to be put equal to 0.9982.

Acid gum:

$$s_{20} = 10.7 \text{ S},$$

$$D_m = 2.4 \cdot 10^{-7} \text{ and } D_A = 2.1 \cdot 10^{-7} \text{ cm}^2/\text{sec},$$

$$V = 0.612,$$

[1] pH of 0.5 per cent solution.

giving

$$M_m = 279\,000 \text{ and } M_A = 319\,000$$

according as the calculation is performed with D_m or D_A.

Sodium gum:

$$s_{20} = 10.4 \text{ S},$$

$$D_m = 2.7 \cdot 10^{-7} \text{ and } D_A = 2.5 \cdot 10^{-7} \text{ cm}^2/\text{sec},$$

$$V = 0.621,$$

giving

$$M_m = 247\,000 \text{ and } M_A = 267\,000.$$

There is a rather surprising agreement between these molecular values and those reported by Oakly for electrodialysed gum (245 000—286 000). This fact may be a mere accident, of course, as we know nothing about the origin of the two samples of gum. Moreover the osmotic pressure method gives a number average molecular weight while the method used in the present investigation gives a weight average, the two values being identical only if the material is homogeneous, otherwise the number average is smaller. To judge from the diffusion measurements, however, there seem to be no large differences in particle sizes, at least for sodium gum. Both methods give smaller molecular weight values for sodium gum than for acid gum. This fact strongly indicates some kind of aggregation or at least some strengthened interaction between the particles in an acid medium. Pectic substances behave in quite the same manner. It may be recalled that the gelling power of the latter substances asserts itself only in acid medium (pH about 3), probably owing to just the same tendency to particle interaction.

Sedimentation Equilibrium.

So far only one experiment of this kind has been performed. In order to protect the gum as far as possible from autohydrolysis during the rather long period, about ten days, needed for the attainment of equilibrium, the gum was neutralized with 0.1 N-NaOH and the medium, 0.2 N-NaCl, was adjusted to pH 7. The concentration and molecular weight distribution

in a 0.5 per cent solution can be seen from Table 6. Rotor speed: 3 600 r. p. m. Temperature: 20° C. x indicates distance in cm from centre of rotation.

Table 6. Sedimentation Equilibrium.

	x	Concentration, per cent, c_i	M_i
Meniscus	5.45	0.187	234 000
	5.50	0.217	250 000
	5.55	0.253	266 000
	5.60	0.298	274 000
	5.65	0.354	279 000
	5.70	0.421	287 000
	5.75	0.507	301 000
	5.80	0.617	321 000
	5.85	0.760	332 000
	5.90	0.980	333 000
Bottom of cell	5.94	1.116	331 000
			$M_w = 307\,000$

The values of M_i have been calculated from formula (2), p. 511, and are to be considered as average molecular weights at the different positions in the centrifuge cell. The mean molecular weight of the substance is found by aid of the formula

$$M_w = \frac{\Sigma\, c_i M_i}{\Sigma\, c_i}$$

the index w denoting a weight average.

The value thus calculated is somewhat larger than that obtained for the same substance (sodium gum) from sedimentation and diffusion. No farreaching conclusions should be drawn, however, from this one experiment. For the moment it may only be said that there seems to be fair agreement between the molecular weight values obtained by the two sedimentation methods.

Autohydrolysis.

As was mentioned in the introduction, the pentose units of the gum are easily split off on hydrolysis and a degraded gum is left. The degradation on heating a ten per cent solution of pure acid gum on the waterbath was followed polarimetrically by Smith (7). The following figures were obtained:

Time of heating:	0	10	22	29	34 hours
$[\alpha]_D^{20°}$	−28°	+22.5°	+40.5°	+41.5°	+42.5°, constant for 12 hours

A similar process of hydrolysis was studied in the present investigation. A 3.8 per cent solution of acid gum in water, having a pH of 2,4, was heated under reflux in the steam from a water-bath and samples taken 3, 6, 9, and 24 hours after the beginning of the process. The samples were diluted ten times with 0.2 N-NaCl and the sedimentation constant of the substance determined. The following figures were obtained:

Time of heating:	0	3	6	9	24 hours
s_{20} in S-units:	9.5	5.8	3.6	2.5	No measurable sedimentation after two hours at 40 000 r. p. m.

This means that hydrolysis under the conditions described for twenty four hours has brought about a splitting of the gum molecules into fragments of molecular weights not higher than about 10 000. Smith (14) mentions that osmotic pressure measurements on methylated degraded gum gave a value of about 4 800. In any case it is quite clear that the stability of the gum molecule is in no way comparable with that of such polyuronides as fruit pectin and alginic acid. The latter, for instance, according to Hirst and Jones (15), may be boiled with dilute mineral acids or heated with water in a closed vessel to 150° C. without any measurable hydrolysis taking place. The existence of branched chains in the gum molecule (cf. Fig. 1) and the prevalence of 1 : 6 and 1 : 3 links, as distinct from the probably unbranched chains and 1 : 4 links of pectic substances and alginic acid, are facts which will contribute to the explanation of these differences.

Summary.

1. A sample of purified gum arabic has been investigated with regard to its behavior on sedimentation and diffusion, with a view to determining its molecular weight.
2. From values of the sedimentation and diffusion constants and the partial specific volume, molecular weights of the order 280 000—300 000 were calculated for acid gum and 250 000—270 000 for sodium gum. From sedimentation equilibrium the mean molecular weight 300 000 was obtained for sodium gum.
3. Autohydrolysis of acid gum on the water-bath was followed by measurements of the sedimentation constant of the splitting products. Hydrolysis for 3 hours reduced the sedimentation constant of the substance to about 60 per cent of its initial value. After 24 hours no measurable sedimentation could be observed.

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The Molecular Weight and Light Absorption of Crystallized Lactoperoxidase.

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Theorell and Åkeson recently described the preparation and properties of a highly purified milk peroxidase (lactoperoxidase, L. P. O.) (1), and somewhat later succeeded in crystallizing the pure material (2). It seemed to be of some interest to determine the molecular weight of the lactoperoxidase by the aid of the methods developed in the Institute of Physical Chemistry in Uppsala, because it would then be possible to calculate from the iron content how many hemin groups each molecule contained. The hemin of the lactoperoxidase is a mixed-coloured one of unknown constitution, and it was thus impossible in this case to make a colorimetric hemin determination, e. g. as pyridin-hemochromogen. The iron content of a not quite pure preparation was 0.0755 per cent (1), but it seemed possible that this figure might by the final purification be either increased, if the impurities were iron-free, or decreased, in the opposite case. The second possibility seemed more probable, since the lactoperoxidase is stubbornly accompanied by a red-coloured protein (1), which has a comparatively high iron content (3).

The material used in determining the sedimentation and diffusion constants was crystallized and recrystallized. It was electrophoretically uniform, and the solubility in ammonium sulphate solutions indicated a high degree of purity (2). The partial specific volume was determined in salt-free solution (10 ml. 0.72 per cent dry weight). Its value was 0.764, which is somewhat higher than the average for the proteins.

Sedimentation Analyses.

Four determinations of the sedimentation constant in the oil turbine ultracentrifuge were carried out in the pH-region from 4 to 11. The isoelectric point of the L. P. O. is situated at pH = 7.7 (2). The results are given in Table 1.

Table 1.

59 000 r. p. m. corresponding to a centrifugal force 250 000 times gravity. LAMM's scale method.

Experiment No.	Content of L. P. O. in solution	Molarity of buffer substances	pH	s_{20} in SVEDBERG units
1	1 per cent	0.076 M-HOAC + 0.017 M-NaOAC + 0.20 M-NaCl	4	5.27
2	» » »	0.05 M-KH_2PO_4 + 0.05 M-Na_2HPO_4	6.8	5.46
3	» » »	0.0067 M-NaH_2PO_4 + 0.06 M-Na_2HPO_4	7.7	5.36
4	» » »	0.023 M-Na_2HPO_4 + 0.005 M-Na_3PO_4	11.0	5.38
			Mean value	5.37

No indication of inhomogeneity was observed.

Diffusion Analyses.

These were carried out according to LAMM (4, 5) with 1 per cent L. P. O. in the buffer solution:

0.0067 M-NaH_2PO_4 + 0.06 M-Na_2HPO_4 pH 7.7, at 20° C.

Experiment 1:

Average value from 7 exposures, 1—4 days, $D_m = 5.92 \cdot 10^{-7}$, $D_A = 6.04 \cdot 10^{-7}$.

Graphical interpolation gives $D_m = 5.83 \cdot 10^{-7}$, $D_A = 6.02 \cdot 10^{-7}$.

Mean value: $D_{20} = 5.92 \cdot 10^{-7}$.

Experiment 2:

Average value from 3 exposures, 3—4 days after start,
$D_m = 5.93 \cdot 10^{-7}$, $D_A = 6.04 \cdot 10^{-7}$.

Graphical interpolation gives $D_m = 5.92 \cdot 10^{-7}$, $D_A = 6.06 \cdot 10^{-7}$.

Mean value: $D_{20} = 5.99 \cdot 10^{-7}$.

D_m is the diffusion constant calculated by the aid of the "moment method", D_A the constant calculated by the aid of the "area method" (cf. GRALÉN (6)).

A homogeneous protein should give the same value for D_m and D_A. An inhomogeneity should give $D_m > D_A$. Our determinations of the diffusion constant of the L. P. O., on the contrary, gave D_A slightly higher than D_m, but the difference is within the limit of error. Thus we are justified in saying that our diffusion experiments tend to indicate the homogeneity of the material.

The molecular weight was calculated according to SVEDBERG's formula

$$M = \frac{R\,T\,s_{20}}{D_{20}(1 - V\varrho)}.$$

The value obtained was $M = 92\,700$.

The frictional ratio f/f_0, calculated according to the formula (7)

$$f/f_0 = 10^{-8}\left(\frac{1 - V\varrho}{D_{20}^2\, s_{20}\, V}\right)^{1/3}$$

was = 1.18. The lactoperoxidase molecule is thus not spherical. If it be supposed to have the shape of an oblong rotational ellipsoid, the ratio between the long and the short axes is = 4:1; if the molecule is hydrated, the ratio is < 4.

Iron Determinations.

Since only 8 mg. of the pure material was left, the iron determinations had to be carried out by a micro-modification of the method of LORBER (8). The combustion was accomplished in glass tubes, 100×17 mm, 0.05 ml concentrated sulphuric acid and 0.05 ml perchloric acid were added to the dry sample.

The temperature in the sand bath was 275—300° C; the combustion was complete after 3 hours. 0.1 ml of redistilled hydrochloric acid, 22 per cent, was added, and the tubes were kept at 100° in a water bath for 30 minutes. 1 ml of water, 0.05 ml 20 per cent sulphosalicylic acid and an excess of strong ammonia were added, whereupon the volume was made up to 2.0 ml with water. The yellow colour was read in microcuvettes, $d = 5$ cm, in the PULFRICH photometer, filter S_{47}. Results:

Table 2.

Sample	Extinction coefficient	Fe in per cent
Blank	0.008	
2 γ Fe	0.408	
3 γ Fe	0.596	
4 γ Fe	0.752	
3.725 mg L. P. O. . .	0.508	0.068
4.350 » » . .	0.626	0.072
		Mean 0.070

One atom of iron per molecule of $M = 93\,000$ would require 0.060 per cent Fe. The material thus contained a trace of foreign iron. The possibility of 2 hemin per molecule would require 0.120 per cent iron, which is obviously out of the question. As mentioned above, it was very difficult to remove the last traces of the red iron-containing protein. Less pure fractions sometimes gave up to 0.112 per cent iron without showing any higher light absorption per unit dry weight. It thus seems justified to conclude that every molecule of L. P. O. contains one molecule of hemin, which is the same content as in the horse-radish peroxidase where $M = 44\,000$ (9).

Light Absorption.

A preliminary light absorption curve was reported previously (1). The absorption of the pure, crystallized material was now determined in the photoelectric apparatus according to WAR-

BURG and NEGELEIN (10). The molar absorption coefficient, β, was calculated on the basis of the dry weight of the dialysed solution and $M = 93\,000$. The results are given in Table 3 and Fig. 1.

Table 3.

λ in mμ	$\beta \cdot 10^{-7}$	λ in mμ	$\beta \cdot 10^{-7}$	λ in mμ	$\beta \cdot 10^{-7}$	λ in mμ	$\beta \cdot 10^{-7}$	λ in mμ	$\beta \cdot 10^{-7}$
690	0.50	590	1.71	490	2.62	390	15.0	290	24.5
680	0.57	580	1.65	480	2.55	380	11.8	280	32.6
670	0.72	570	1.62	470	2.70	370	10.4	270	29.4
660	0.82	560	1.69	460	2.98	360	9.15	260	21.9
650	1.09	550	1.86	450	3.43	350	8.67	250	17.6
640	1.36	540	1.90	440	4.98	340	7.27	240	24.4
630	1.52	530	1.99	430	9.80	330	6.02		
620	1.57	520	2.32	420	16.2	320	5.10		
610	1.67	510	2.54	410	25.2	310	5.02		
600	1.74	500	2.63	400	19.6	300	6.95		

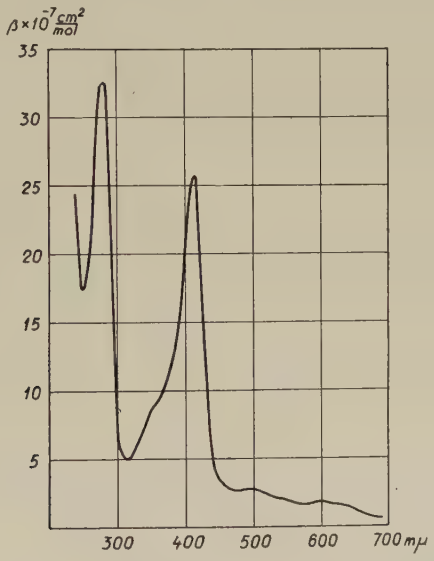

Fig. 1. Light absorption of lactoperoxidase.

The shape of the curve is essentially the same as that of the preliminary one. The absolute values are now somewhat

higher, which depends on the fact that the values of the preliminary curve were calculated on the basis of the iron content 0.0755 per cent, which obviously included some foreign iron.

The maximum 280 mμ is somewhat lower compared with the Soret-band (412 mμ, $\beta = 25.7 \times 10^7$) in the pure material, as was to be expected. The absolute values of β are of the usual order of magnitude for a ferrihemin-proteid, which gives further support to the assumption of one hemin per molecule.

Summary.

Recrystallized lactoperoxidase was submitted to sedimentation, diffusion, light absorption and iron analyses. The material was found to be homogeneous in a physico-chemical respect.

The molecular weight was 93 000, the sedimentation constant $s_{20} = 5.37$ S, the diffusion constant $D_{20} = 5.95 \cdot 10^{-7}$, the partial specific volume $V = 0.764$, the frictional ratio $f/f_0 = 1.18$.

The iron content was 0.070 per cent, slightly higher than expected for 1 Fe per molecule, 0.060 per cent. The difference is due to a contamination with foreign iron.

The light absorption coefficients in the wave length region 2 400 — 6 900 A units are given.

Our thanks are due to Professor The Svedberg for the opportunity of performing ultracentrifugal and diffusion experiments in the Institute of Physical Chemistry, Uppsala.

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Studies on Macromolecular Components in Faeces and Intestinal Contents.

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In previous papers by Tiselius and Gard (1) and Gard (2, 3), the isolation and a preliminary description of heavy components in faeces and intestinal contents were reported. The substances in question were found during attempts at purification of poliomyelitis virus from the sources mentioned. From a physicochemical point of view as well as in electron micrographs, no distinct differences were detected between the intestinal components and the virus itself as isolated from infected nervous tissue. In specimens displaying viral activity this biological effect seemed to be associated with the fraction containing the filamentous macromolecular component. However, an identical substance was present also in faecal specimens without demonstrable virus activity and as far as the present observations go it must be regarded as regularly occurring in the intestinal contents, at least in adults. Evidence was presented to show that the macromolecular component was a nucleoprotein. On account of the undeniable similarity of the intestinal heavy protein to the poliomyelitis virus the hypothesis was advanced that the protein was an inactive or rather non-neurotropic form of the virus. At all events, further studies of this substance and its relation to the virus were necessary. A similar or possibly identical substance was found in a few species besides man and the white mouse, viz. the pig and the brown wild rat (*Mus decumanus*). It was deemed advisable to start the study on material from the brown rat, known to be resistant against spontaneous or experimentally induced poliomyelitis infection.

I. Purification (S. Gard).

The first step consisted in securing larger quantities of the substance in a pure state. In this large scale purification a somewhat modified procedure was adopted.

A number of adult rats were kept in cages bottomed with wire netting and without litter of any kind. The faeces were collected on tin trays which were emptied twice weekly and the samples treated immediately. A certain amount of 0.05 M NaCl solution was added and the mixture shaken with glass beads in a shaking machine for 4 hours. Then further NaCl solution was added to make a 5 per cent suspension and the mass was extracted by mechanical stirring for a further 8 hours. It was then left to sediment over night. The supernatant was siphoned off and run twice through a De Laval industrial separator used as a clarifier. The effective centrifugation time was about 20 minutes in a field of 5 000 times gravity. The clarified extract was precipitated with ammonium sulphate to a total concentration of 33 per cent saturation. The precipitate was filtered off with Hyflo Supercel and the clear filtrate discarded. The precipitate was extracted with half the original volume of distilled water and again filtered with filter-aid. The filtrate was yellow in colour and opalescent. It was concentrated about ten times by ultrafiltration. The concentrate was run in a Beams centrifuge at 27 000 r. p. m. for 2 hours. The clear supernatant was discarded. The precipitate was left to swell over night in distilled water and then redissolved to the original volume in distilled water. The solution was run "up-and-down" to 16 000 r. p. m. The precipitate was washed once in the centrifuge and the washings added to the supernatant. This cycle of high and low speed centrifugation was repeated three times, the centrifugation time at 27 000 r. p. m. being reduced to 90 minutes in the subsequent runs.

After this treatment the preparation formed a yellowish brown solution, transmitting light clearly but showing a strong Tyndall cone. On analysis in the ultracentrifuge, only one component was usually distinguished. Not infrequently, however, two distinct components were present. This was the case principally in preparations that had been precipitated repeatedly with ammonium sulphate. The centrifugation diagrams then had the appearance of Fig. 1. The slower component was identical with the one previously named α, while the faster one seemed to be related to the β component and will be so designated below.

It was previously noticed (3) that the presence of ammonium sulphate in moderate concentrations brought about a change in the appearance of the sedimentation diagrams in a characteristic way and it was assumed that the salt removed some impurities attached to the surface of the filamentous protein molecules. This effect has been further studied. A solution in distilled water of the α component is almost colourless and clear with a distinct although not very pronounced bluish

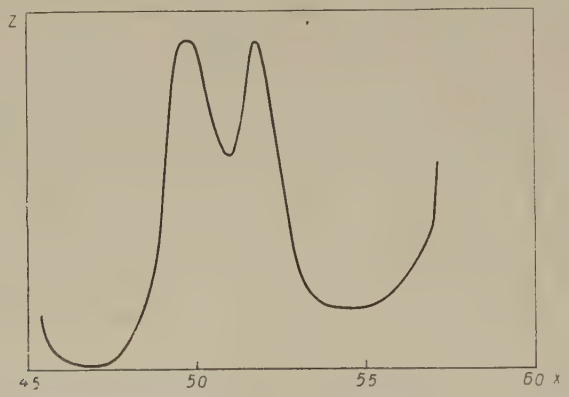


Fig. 1. Sedimentation diagram of partially purified faeces extract. Centrifugal field 11 000 g. Exposure after 30 minutes. LAMM'S scale method.

TYNDALL cone. If ammonium sulphate is added gradually one finds, when the salt concentration amounts to about 0.1 M, a sudden increase in opalescence and the solution assumes the characteristic sheen of suspensions of microcrystals. On microscopical examination of such solutions, minute needles or rods were visible in the dark field. The length of the particles was estimated at about 1 μ. Fig. 2 is a diagram showing the variation of extinction coefficient with the concentration of ammonium sulphate. The transition from sol to "crystalline" state was very sharp. The "crystals" were readily sedimented on low speed centrifugation. Accordingly, the further purification of the extracts was performed as follows.[1]

Ammonium sulphate was added to 5 per cent saturation and the maximum extinction value was awaited. An equilibrium was

[1] In crude extracts no "crystallization" occurs, on account of the presence of mucine that even in minute amounts inhibits completely the appearance of this phenomenon.

seldom reached until after 12 hours. The preparation was then run up-and-down to 16 000 r. p. m. The supernatant was carefully removed with a syringe and the precipitate after swelling redissolved in distilled water. It was then run up-and-down to 16 000 r. p. m. The resulting precipitate was washed once in the centrifuge and the washings added to the supernatant. The preparation was further purified by identical "recrystallization" three times.

The α component thus purified gives an almost colourless solution with a faint bluish Tyndall cone. When centrifuged at high speed it forms a translucent, practically colourless gel.

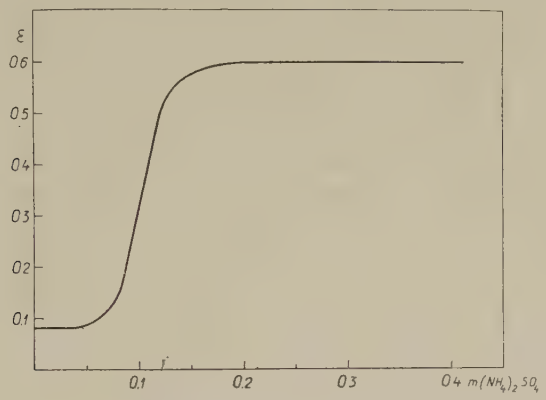


Fig. 2. Variation of extinction coefficient with the concentration of ammonium sulphate in solutions of the pure α component. Readings made in a Pulfrich photometer with filter S 47, absorption maximum at 4 580 Å.

The volume of the gel is two to three times greater when obtained from solutions in distilled water as compared with dilute saline, indicating differences in the degree of hydration. On ultracentrifugal analysis it does not display the inhomogeneity observed in earlier, less pure preparations. The moving boundary in exceedingly sharp, all the way down to the bottom of the cell. Fig. 3 shows a sedimentation diagram of a pure preparation. A definite value of the sedimentation constant could not be obtained. A salt-free solution with a concentration of about 0.1 per cent gave a constant of $s_{20} = 130$ S (Svedberg units). On addition of NaCl to 0.01 molarity, the constant increased to 190 and remained at this level on further addition of NaCl. This phenomenon must be regarded as a

charge effect. — When the salt concentration was kept constant, the rate of sedimentation was found to be dependent upon the concentration of the protein. In the range tested, the lower limit being set by the capacity of the optical registration method at about 0.01 per cent, this dependence seemed not to stabilize. It was not rectilinear as is the case with tobacco mosaic virus, nor was the usual formula applicable.[1] Obviously, even in solutions of 0.01 per cent inter-

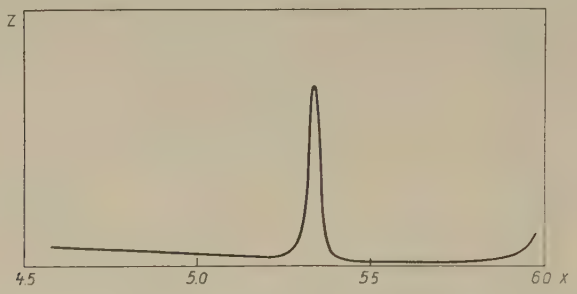


Fig. 3. Sedimentation diagram of the pure α component. Centrifugal field 11 000 g. Exposure after 270 minutes. LAMM'S scale method.

molecular forces are in play and the state of ideal solution not yet attained. Extrapolation of the concentration-sedimentation curves is, therefore, not feasible. The end value might be estimated at about $s_{20} = 250$ S, but this value cannot serve as a basis for calculations.

The mother liquors from the "crystallizations" were combined, concentrated by ultrafiltration and run down in the centrifuge at 27 000 r. p. m for 90 minutes. The brown pellicles were redissolved in distilled water. When ammonium sulphate was added to 5 per cent saturation, the characteristic sheen reappeared, although the original supernatant had not shown this feature. By low speed centrifugation an additional amount of the α component could be secured. When this procedure was repeated over and over again the total yield of α component gradually increased whereas the amount of residual β component decreased. It is not yet definitely established whether or not a stable macromolecular substance different from the α component can be extracted from preparations of the β component. In supernatants

[1] The relation between sedimentation constant s and concentration c often has the form $s_c = s_0 \cdot \frac{1}{1 + k\,c}$, where k is a constant.

from the high speed centrifugations small amounts of a substance were detected, which on ultracentrifugal analysis appeared homogeneous with a sedimentation constant of from 30 to 60 in different runs.

It seems probable, therefore, that the β component in successive treatments with ammonium sulphate is split into two distinct substances, one of which has the properties of the α component. This question must, however, be submitted to further study.

II. Electron-Optical Observations (S. Gard and H. Tyrén).

The instrument used was the "Übermikroskop" of *Siemens und Halske A. G.* with electromagnetic lenses. The field of acceleration was 100 kV, the resolving power 3.5 mμ and the magnification applied 20 000 : 1.

For observations on the α component in distilled water, a range of concentration of from 10^{-6} to 10^{-8} g per ml was found most suitable. The pictures obtained were fairly uniform. Filaments of the type previously described (1, 2, 3) were the only structures observed. They gave the impression of being very flexible, were usually delicately curved and not infrequently showed branching, probably by apposition (Fig. 4). The length of the filaments was often considerable, threads of 3—4 μ sometimes being measured. The thickness was very uniform. It was measured on the plates as about 15 mμ. The filaments were usually loosely arranged; true net formation was not very prominent. The net-like pictures observed (Fig. 5) seemed to have arisen through superposition of branched filaments rather than through gel formation. Formation of bundles of the type previously described occurred occasionally. In all probability this phenomenon is an artifact, appearing during the desiccation of the object. It may be assumed, therefore, that the α component appears in salt-free solutions as single filaments without lateral association and without gel formation. In low concentrations a tendency of the long threads to dissociate into smaller units was evident.

Specimens containing ammonium sulphate gave a different picture. The minute "crystals" observed in the light micro-

scope appeared as irregular spindle-shaped bodies, 1—1.5 μ in length and 0.1—0.15 μ in breadth (Fig. 6—7). They were often fringed at the ends or sometimes twisted as in Fig. 7, showing their origin as associated filaments. It is quite obvious that these bodies cannot be true crystals. Nevertheless there seems to be a certain regularity in their structure. They might be comparable to the tactoids appearing in sufficiently pure and concentrated preparations of tobacco mosaic virus. In solutions containing 0.12 M ammonium sulphate there appeared, besides the bodies now described, occasional long single filaments and a remarkably large number of short rods measuring about 150 mμ (Fig. 6, 7), obviously corresponding to the single molecules as previously described. More concentrated solutions showed a dense gel structure where the tactoids were represented by short thick bars, connected by branches of single threads (Fig. 8).

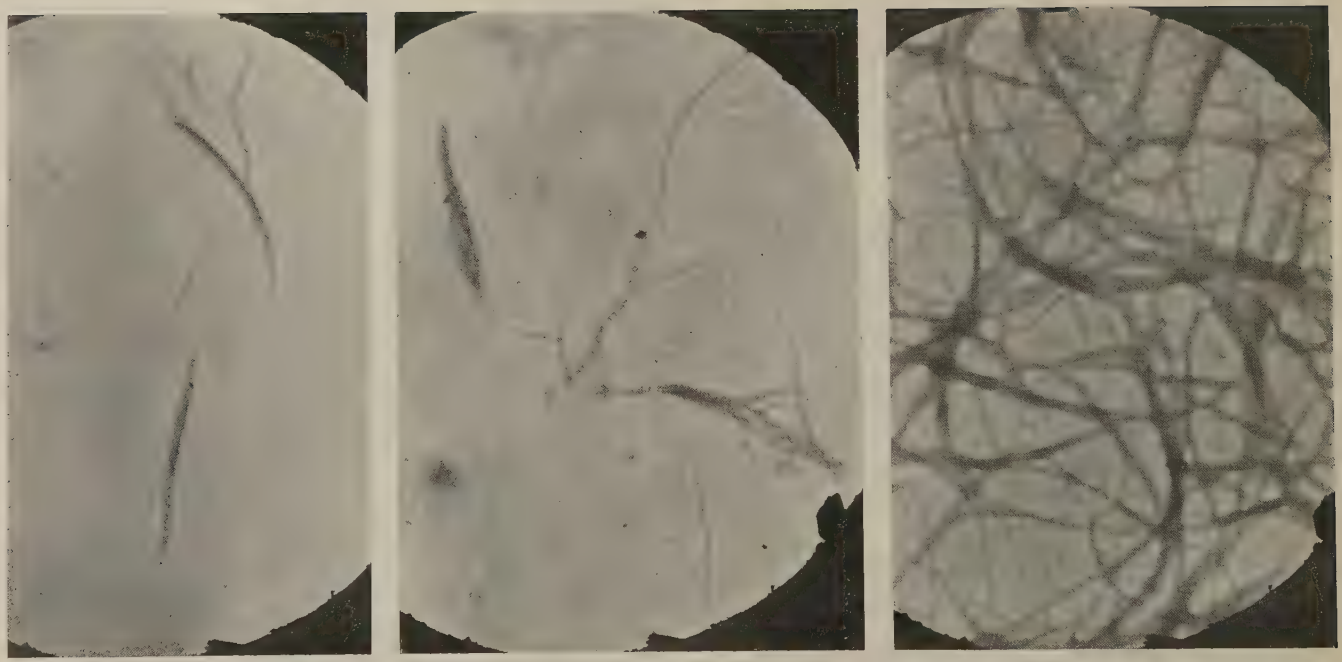
Preparations of the β component contained filaments of a similar type; they were curved and had the same thickness. The arrangement was, however, distinctly different. True net formation was the rule; single threads were seldom observed (Fig. 9—10). The nodes and intersections were often enlarged by agglomeration of amorphous low-molecular material. The pictures gave the impression that the filaments were "glued" together. Sometimes particulate material of a higher contrast was found included in the agglomerations.

III. Measurements of Stream Double Refraction (S. Gard and O. Snellman).

The measurements were carried out in the apparatus and according to the methods described by Snellman and Björnståhl (4).

Preparations previously studied in this respect gave values for the particle length of about 600 mμ, although the curves obtained indicated a certain inhomogeneity probably due to the presence of impurities. Specimens purified as described above were, however, satisfactorily homogeneous. The results of the measurements are graphically illustrated in Fig. 11. It might be mentioned in this connection that similar prepara-

Figs. 4 and 5. The pure α component in distilled water. Concentration 10^{-7} g per ml. Magnification 30 000 : 1, electron optically 20 000 : 1.



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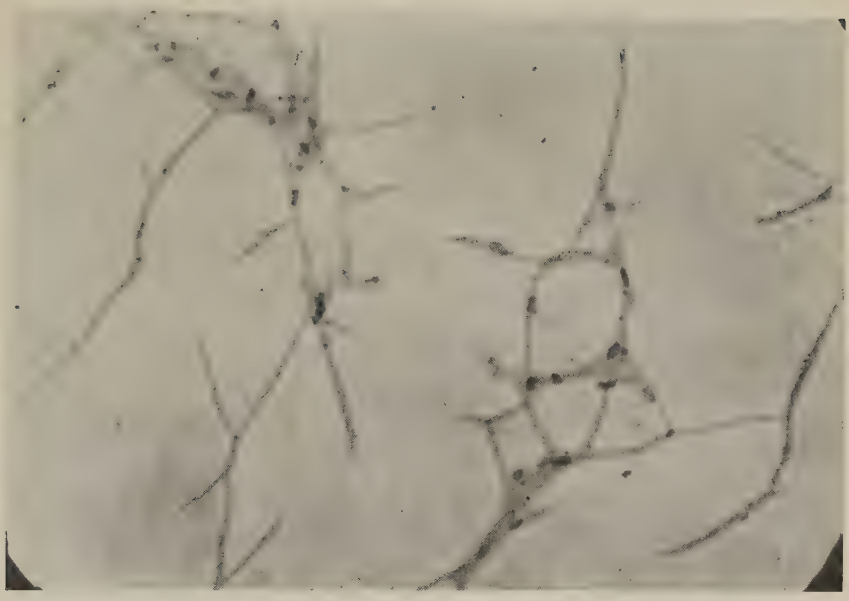
Figs. 6 and 7. The pure α component in 0.12 M ammonium sulphate. Concentration 10^{-7} g per ml. Magnification electron-optically 20 000 : 1. — Fig. 8. The pure α component in 0.12 M ammonium sulphate. Concentration 10^{-5} g per ml. Magnification electron optically 20 000 : 1.



Figs. 9 and 10. The β component in distilled water. Magnification 30 000 : 1, electron optically 20 000 : 1.

tions from human stools examined by Melnick (5) failed to show anisotropy of flow. His negative findings must be attributed to the obviously low degree of purity of the preparations and possibly to insufficient sensitivity of the optical device.

Solutions of the α component in distilled water displayed a measurable double refraction in concentrations down to

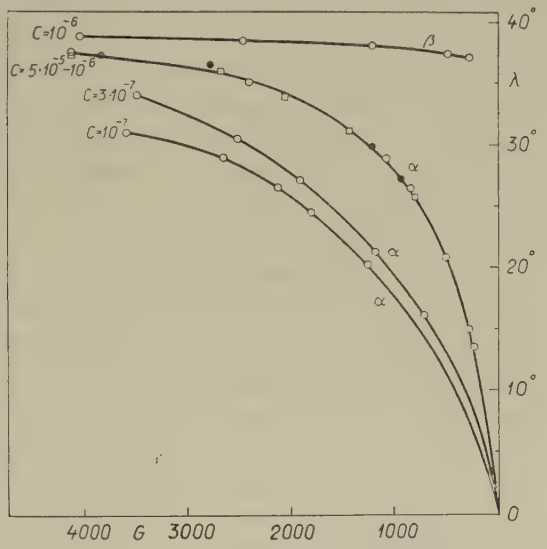


Fig. 11. Stream-double refraction. Variation of the angle of extinction with the velocity gradient in solutions of the α and β components.

10^{-7} g per ml. In the interval 10^{-4} to 10^{-6} g per ml the variation of the angle of extinction with the velocity gradient indicated that the particle length was uniform and about 600 mμ. In concentrations below this range, the curves obtained corresponded to a particle length decreasing with the concentration. A new equilibrium was not yet attained when the limit of measurability was reached at 10^{-7} g per ml. The particle length in solutions of this concentration may be estimated at about 450 mμ.

These results are not in complete agreement with the electronoptical observations. In the micrographs, the length of the filaments is far from uniform and considerably exceeds 600 mμ. It must be remembered, however, that the method

of preparing the objects is not suited to preserving the original state of the solution. During the desiccation, a gradual change of the concentration takes place, during which association phenomena may occur. We are, therefore, inclined to consider the results of the stream double refraction measurements as more adequate as far as the conditions in dilute solutions are concerned.

The dissociation of the particles in very dilute solutions is an interesting phenomenon. In studying mouse poliomyelitis, Gard (3) found, when very small inocula were used, a distribution of "takes" that was best interpreted as evidence of a dissociation of the virus particles with increasing dilution of the specimen. It has not been possible to confirm this theory by ultracentrifugal or diffusion measurements. Under the conditions of the biological experiments, however, concentrations of an order of magnitude of 10^{-12} to 10^{-13} g per ml were used, whereas the lower limit in the physico-chemical measurements mentioned is about 10^{-4}. The substance in question here is certainly not identical with the virus. Whatever its relationships to the biologically active substance may be, with respect to physico-chemical properties it closely resembles the virus. It is, therefore, of special interest to establish that the α component shows a dissociation phenomenon but only in concentrations far below the interval attainable in centrifugation and diffusion studies. Why the dissociation does not set in at higher concentrations is still obscure. It might have a connection with the fact that more concentrated specimens do not behave as ideal solutions, as indicated by the ultracentrifugal data. On the other hand, the stream double refraction curves do not suggest a gel formation in the interval of concentration studied. Further observations are necessary for the elucidation of these conditions.

The β component showed, in the interval of velocity gradients applied, an angle of extinction that was practically constant and very close to the direction of flow. This type of curve is characteristic of gel structures. The result of the measurements is in full agreement with the electron-optical observations. All micrographs of the β component showed true net formations. Considering the evidence obtained by different

methods it seems justifiable to assume that this component is an adsorption compound of the α component and some low molecular substance. This question is being further studied.

Summary.

The purification of a macromolecular substance from the faeces of wild brown rats is described. Under natural conditions this substance, called the α component, seems to be combined with some low molecular material to form an adsorption compound. This compound can be split by repeated treatment with dilute ammonium sulphate solutions. The pure α component appears as flexible filaments, about 15 mμ in breadth. In dilute ammonium sulphate solution it forms "crystallites" or tactoids of a fairly uniform size of 1—1.5× 0.1—0.15 μ. Stream double refraction measurements proved to be a valuable and very sensitive method in studying the nature of dilute solutions of this substance. The results indicated a particle length of about 600 mμ in concentrations down to 10^{-6} g per ml, below which a dissociation into shorter particles begins.

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An Attempt at Physico-chemical Analysis of Protein Antigens Isolated from the Tubercle Bacillus.

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In studying the serological and immunological reactions in tuberculosis, it is important to give a chemical and physico-chemical definition to antigenic substances. This holds also true for the proteins of the tubercle bacillus.

The investigations in this field have dealt with the proteins of the tubercle bacillus itself and with those proteins excreted by the bacilli into the culture medium, which are known as tuberculin. Tuberculin has been extensively investigated by Seibert (1, 2, 3, 4, 5) and her co-workers, and it is at present the best known group of tuberculoproteins. It would be decidedly advantageous to have a similar collected knowledge of the cellular proteins.

The investigations by Seibert have shown the difficulties in fractioning tuberculin and in defining its components. When working with the whole protein system of an organism, one must expect very complicated conditions. The only biological protein mixtures known to be fairly definable are preformed body-fluids i. e. blood serum. Cell and tissue extracts are extremely non-homogeneous. Widström (6) has made attempts to study water extracts of tubercle bacilli by ultracentrifugation and electrophoresis with rather discouraging results.

Menzel and Heidelberger (7) have worked with another method and fractionated the cellular proteins by successive extractions with solutions of increasing alkalinity. These fractions were sub-fractioned with ammonium sulphate or

sodium sulphate. They concluded that there are at least three different antigenic proteins in the tubercle bacillus. But it is evident, that it has not been possible to effect a complete separation with the applied fractionation methods. In the experiments described below it is interesting to notice that the fractions extracted with alkaline solutions were chemically and serologically different from those extracted with acid or neutral solutions. It was even shown, that these characteristics were not a result of the alkali treatment. This "alkali soluble" protein of the tubercle bacillus has been described by several authors and by Umezu and Wagner-Jauregg (8) as a part of the so called "Gerüstsubstanz". The present investigation is devoted to this fraction, because it seemed more likely that it could be obtained in a homogeneous form than any other protein fraction. All other fractions are to be separated out of what is known to be an extremely non-homogeneous mixture, and this one is to be split off from an insoluble substance by mild alkaline treatment. The preliminary results of an investigation into this fraction are reported below.

Tubercle bacilli of a B. C. G.-strain were grown on a synthetic medium. After three weeks, they were killed by freezing and drying according to the "lyophil"-method and ground for eight hours in a ball-mill of stainless steel at a temperature of — 60 to — 70° C. After grinding, the material was collected and extracted with physiological NaCl-solution and alcohol-ether according to the following scheme (Table 1) until constant solubility expressed in dissolved amount of nitrogen was obtained. Before the extraction the dry weight was 31.558 g. and the nitrogen content 6.3 per cent.

After these extractions the residue was frozen and dried. After drying, it weighed 16.655 g. and the nitrogen content was 8.3 per cent. Accordingly 47 per cent of the dry weight and 31 per cent of the nitrogen content were removed by the extractions.

In order to investigate the possibilities of extracting the nitrogenous fraction of this residue, extraction was tried under different conditions. The results of extraction with water at varying hydrogen ion concentration and varying amounts of suspended residue are collected in Tables 2—4.

Table 1.

Extraction	Time of extraction in hours	Volume of extract in ml.	Nitrogen content of extract in mg./ml.	Nitrogen extracted in mg.
Water extract No. 1	1	275	0.010	276
» » » 2	1	450	0.317	143
» » » 3	1	450	0.184	82.8
» » » 4	1	450	0.072	32.4
» » » 5	1	450	0.105	47.3
Alcohol-ether extract	24	500	—	—
Water extract No. 6	1	300	0.125	37.5
			Total nitrogen extracted	619.0

The solubility reaches a minimum at neutral reaction. It increases a little in acid solutions and very markedly in alkaline solutions (Table 2). In 0.05 N- and 0.10 N-NaOH it is about ten times as high as in physiological NaCl-solution.

Table 2.

Extraction fluid	Solubility mg. N/ml.	Extraction fluid	Solubility mg. N/ml.
0.2 N-HCl	0.032	0.001 N-NaOH	0.011
0.1 N-HCl	0.033	0.01 N-NaOH	0.020
0.01 N-HCl	0.031	0.1 N-NaOH	0.345
0.001 N-HCl	0.030	0.2 N-NaOH	0.430

Temperature 20° C.
Time of extraction 24 hours.
Suspended residue: 0.25 g. pr 10 ml.

Table 3 shows the solubility of one preparation in physiological NaCl-solution at varying amounts of suspended residue.

The solubility in physiological NaCl solution increases with increasing quantity of suspended residue and is roughly proportional to the latter. This suggests that the residue contains at least two components — an insoluble main part and a smaller soluble part, or that in solutions the soluble ma-

Table 3.

Suspended residue in g. pr 10 ml.	Solubility in mg. N/ml.
0.06	0.005
0.12	0.021
0.25	0.037
0.50	0.074
0.75	0.134

Temperature 20° C.
Time of extraction 24 hours.

Table 4.

Suspended residue in g. pr 10 ml.	Solubility in mg. N/ml.
0.06	0.097
0.12	0.202
0.25	0.407
0.43	0.700
0.50	0.805

Temperature 20° C.
Time of extraction: 24 hours.
Extraction fluid: 0.05 N-NaOH.

terial is split off from the residue. In the latter case the two components may form a dissociable component system, according to Sörensen (9). In alkaline solutions also the solubility depends on the amount of residue present. This is demonstrated in Table 4.

According to this result a considerable part of the residue may be extracted in alkaline solution. If this treatment does not alter the chemical and physico-chemical properties of the extracted compounds, such solutions may serve as an object of investigation into the alkali-soluble antigens from the tubercle bacillus.

A large number of extractions have been made with 0.05 N- and 0.10 N-NaOH at room-temperature and at 4° C. Ultracentrifuge experiments have shown that it is possible to get

extracts relatively homogeneous, providing the extraction-time is short and the extracts are investigated immediately after extraction. When stored a day or two they are altered and the molecules aggregate and precipitate. The sedimentation diagrams have shown the extracts to contain a main component with a low sedimentation-constant and in different preparations a varying quantity of polydisperse high molecular

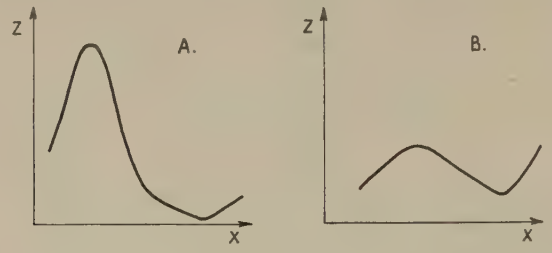

Fig. 1. Sedimentation diagrams of alkali soluble tuberculoprotein.
A. 55 minutes after full speed. B. 150 minutes after full speed.
Abscissa: Distance from centre of rotation.
Ordinate: Displacement of scale line.

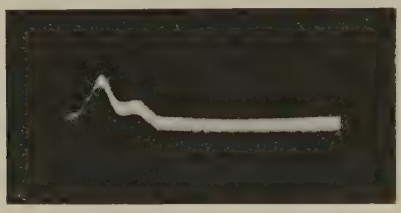

Fig. 2. Electrophoresis diagram of alkali soluble tuberculoprotein.
Exposure 100 minutes after starting.

compounds (Fig. 1). The sedimentation constant s_{20} of the main component was determined and 0.78 S (Svedberg units) was found as the mean value for ten determinations.

The sedimentation has been studied in the Svedberg ultracentrifuge (10) rotating at a speed of 69 000 r. p. m. (centrifugal force of about 340 000 times gravity). It was impossible to determine the diffusion constant in the very unstable solutions, and for this reason we have not been able to calculate the molecular weight.

In the electrophoresis apparatus of Tiselius (11) the extracts proved to contain two or three fractions, both being

negatively charged at pH 6.8. Fig. 2. shows the diagram after 100 minutes electrophoresis in phosphate-buffer of a solution containing 0.72 mg. N pr ml. at pH 6.8, $\mu = 0.10$ and a potential gradient of 5 volt/cm.

A test of the tuberculin potency was carried out. A Standard PPD according to Seibert (3) and an extract were compared in the skin test on tuberculous rabbits infected with avian tuberculosis. Seven animals were tested with three doses of PPD and of the extract on each side of the back. For the extract the content of tuberculoprotein was calculated from the analytically found values of nitrogen. The result is collected in Table 5.

Table 5.

Amount of PPD in mg.	Tub. react. Radius in mm. Mean of 7 animals	Amount tub. protein of extract in mg.	Tub. react. Radius in mm. Mean of 7 animals
0.30	13.9	0.15	14.8
0.075	12.4	0.075	10.8
0.020	4.8	0.020	8.1

From these figures it is evident that the tuberculo-proteins of the extracts are very potent and probably the potency is of the same order as that of Standard PPD.

These results are as yet to be looked upon as preliminary and further reports will later be given elsewhere.

The results seem to be important for different reasons. The attempt to get a physico-chemical definable antigen fraction of tubercle bacilli has been successful. The fraction has a high tuberculin potency, and it has a very low sedimentation constant. Finally the isolation and characterization of this fraction is interesting in connection with other investigations of this laboratory. Viz. Widström (6) has found that the immunizing capacity of ground tubercle bacilli treated with alkali is greater than that of the untreated ones. Therefore it may be possible that this fraction acts as an *immunogen* in the serological reactions of tuberculosis.

The author wishes to thank Professors The Svedberg, Arne Tiselius and John Reenstierna for valuable advice, discussions and for the resources placed at his disposal for this work; and Dr. Anders Wassén for generously providing the B. C. G.-cultures.

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Sulphanilamides and Experimental Tuberculosis.

Some New Approaches.

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The substances which have been tested in tuberculosis in the vain hope that they would destroy the tubercle bacillus without harming the patient may be enumerated as follows: salts or other compounds of calcium, gold, silver, bismuth, mercury, cadmium, manganese, and many of the rare earths; iodine and arsenic preparations, silicic acid, guaiacols and creosotes, quinine derivatives; dyes such as acridine, benzidine, thiazine and triphenylmethane dyes; the fatty acids from chaulmoogra and cod liver oils. This list, however, is by no means complete. Gold, which has no direct bactericidal action on the tubercle bacillus but may act as a stimulant on the reticuloendothelial system, appears from the literature on the subject to have been the most successful of these agents; otherwise no positive results to speak of have been obtained.

The Action of Sulphanilamides and Sulphones.

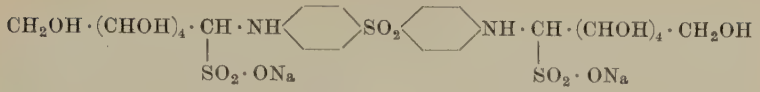
Since the discovery of the sulphanilamides, the experimental research on tuberculosis has also made progress, and a large number of papers have been published describing experiences with the administration of different sulphanilamides to laboratory animals infected with tuberculosis, or with studies *in vitro* of the effect of the sulphanilamides on various strains of the tubercle bacillus on different culture media. Thus many workers have claimed that the common sulphanilamides in high concentrations may modify the course of experimental

tuberculosis in guinea pigs (for the earlier literature see 1, 2). The results have varied greatly, but on the whole it is possible to observe a certain effect. However, no positive clinical results have been secured.

Mycob. tuberculosis is an acid-fast bacillus rich in lipids and fat substances, which amount to 20 to 40 per cent of the dry bacterium (3, 4); the bacterium also appears to be surrounded by a membrane or capsule, according to observations made with the electron microscope (5). This would appear to bear out the theory held by some workers that the cause of the lack of activity is that the contact between the sulphanilamides used and the tubercle bacillus is defective. It has also been attempted to secure better results by introducing lipophilic radicles into the sulphanilamides. On this basis N^1-dodecanoylsulphanilamide has been prepared by Crossley, Northey and Hultquist (6) and tested experimentally, without, however, consistent success (7, 8, 9, 10). Sulphanilamide derivatives of chaulmoogric acid — of additional interest, since this acid in itself shows a certain activity towards *Mycob. leprae*, which is related to the tubercle bacillus — and of other lipophilic acids have also been prepared and tested in animal experiments on leprosy and tuberculosis, but with no effect (10).

On the ground that sulphathiazole is considerably more active against most of the bacteria investigated than sulphanilamide, the introduction of a lipophilic substituent in the heterocyclic part of the former compound has also been tried. A series of alkyl sulphathiazoles (amyl, heptyl, nonyl, etc.) (11), as well as several alkyl sulphathiodiazoles (12), have been prepared in order that they might be tested against the tubercle bacillus. Even if it would appear theoretically that lipid-solubility should increase the contact between a chemotherapeutically active compound and the tubercle bacillus, this has not been proved to be the case. Furthermore, "lipid-solubility" is a comprehensive term, and in the case in point rather specific conditions may be involved.

N^1-dodecanoylsulphanilamide.



Disodium 4,4′-diaminodiphenylsulphone-N,N′-didextrose sulphonate.

Another type of compound, which has attracted great interest, is promin, disodium 4,4′-diaminodiphenylsulphone-N,N′-didextrose sulphonate, first studied by Feldman and Hinshaw (13). In animal experiments promin gave a definite effect (14, 2, 15, 16). Promin is transformed in the organism to 4,4′-diaminodiphenylsulphone, which appears to be more effective (2). Unlike this compound, however, promin is soluble in water. Both compounds obviously have a better effect *in vivo* than the sulphanilamides tested hitherto (17, 2, 18). Since diaminodiphenylsulphone is more active towards many bacteria than the most active sulphanilamides, while it acts in the same manner as these compounds, it is not surprising that its effect is greater with regard to the tubercle bacillus also. Unfortunately the compound is highly toxic, which renders it useless for clinical purposes; the clinical tests of promin have also shown severe secondary effects. A certain therapeutic effect has indeed been noted in a few cases, but has not warranted more extensive testing of the preparation (13, 19, 20, 21). Even if the results obtained so far are disappointing, the experiments are nevertheless remarkable.

Another compound closely related to promin is diasone, disodium formaldehydesulphoxylate-diaminodiphenyl sulphone, recently subjected to testing in animal experiments, in which an effect could be observed (22).

Certain other compounds, not of the sulphanilamide group, investigated in the experiments of the past few years are also worthy of note. For example, diphenylamine and other antioxidants have an inhibitory effect on the growth of tubercle bacilli in different media (23). The same is true of 2,3,5-triiodobenzoate, which inhibits growth and oxygen uptake (24), and 2,4′-dichlorobenzophenone, which is bacteriostatic at very high dilutions (25). All these compounds have been tested *in vitro* only; consequently far-reaching conclusions cannot be drawn as to their effect *in vivo*.

Experimental.

About three years ago we planned at this laboratory the preparation of a few new types of sulphanilamides, with the intention of studying their effect on experimental tuberculosis (26). In this connection we attempted two different modes of increasing the affinity of sulphanilamide for *Mycob. tuberculosis*, at the same time retaining or increasing the chemotherapeutic effect of the compound. The theoretical background of these experiments is discussed in the present paper, and mention is made of some of the compounds which we synthesised. So far nothing can be said as to the bacteriostatic effect on the tubercle bacillus, since the investigation regarding this point is still in progress. These experiments are being carried out *in vitro* and *in vivo* with a virulent human strain.[1] For the experiments *in vivo*, guinea pigs are used.

Meanwhile, in order to understand the building-up of the new compounds, we must keep in mind the connection between the chemical structures and the chemotherapeutic effects of the sulphanilamide derivatives. Substitution at the amido nitrogen, N^1, in sulphanilamide, gives compounds with a greater or smaller effect than that of the parent substance. The derivatives which so far have been of the greatest therapeutic importance, viz. sulphapyridine, sulphathiazole and sulphapyrimidine, are substituted in this manner with a heterocyclic radicle, but a number of N^1-acyclic derivatives also have a greater effect than sulphanilamide. If the amino group is blocked at N^4, however, the compounds become inactive, unless a compound with a free amino group is rebuilt *in vivo*. It is, nevertheless, obvious that the sulphonamide group, which must be in the *p*-position with respect to the amino group, may be altered in many ways without the activity being abolished. It is hardly possible to associate the effect of this group with a definite atomic configuration; it must be that several widely different atomic groups are able to produce the

[1] This part of the investigation is being carried out by A. R. Frisk. The chemical work is being done in collaboration with R. Dahlbom and T. Ekstrand and, for certain syntheses, with E. Berlin. Some of the biological questions have been studied by S. Wiedling.

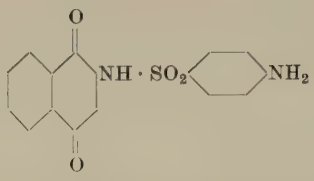
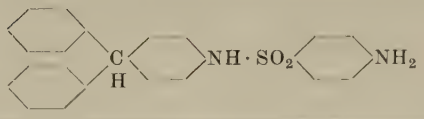
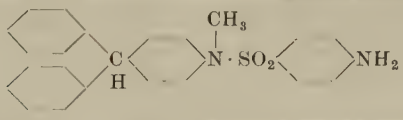
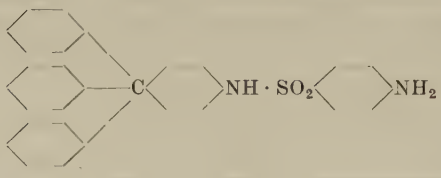
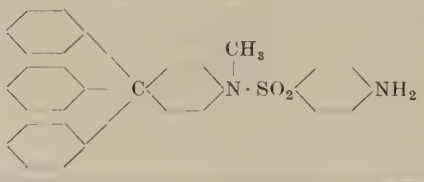
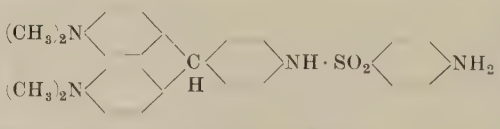
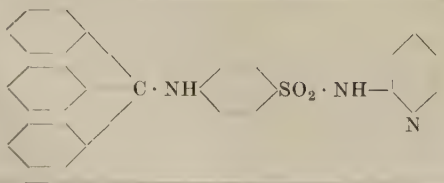
same effect. An attempt has been made to explain the phenomenon from the viewpoint of electron theory (27), without, however, reaching any definite conclusions (28).

Sulphanilamides Substituted with Naphthalene Derivatives.

As has been mentioned above, if it were possible to secure an affinity for the tubercle bacillus, this might conceivably lead to a better contact. Our first attempts in this direction were based on the following facts. A large number of bacteria, including the tubercle bacillus, are able to form compounds of a vitamin K nature (29, 30), and consequently there is reason to believe that compounds of this kind may play a part in the metabolism of the bacteria in question. In addition, such substances are required as growth factors by a bacillus closely related to the tubercle bacillus, namely, *Mycob. paratuberculosis* or JOHNE's bacillus (31). For this reason we synthesised a series of sulphanilamides which are substituted at the amido nitrogen with naphthalene derivatives similar in nature to the antihemorrhagic compounds (32), which are 1,4-naphthoquinone derivatives.

The following examples may be mentioned: 2-sulphanilamido-1,4-naphthoquinone (I; see Table), 2-methyl-1-sulphanilamido-naphthalene (m. p. 248°), and 2-methyl-1-hydroxy-4-sulphanilamido-naphthalene (209° decompn.). The compounds are soluble in various organic solvents, but difficult to dissolve in water. They have been tested against pneumococci of types I and III and against *E. coli*, and their effect has been compared with that of sulphanilamide and other compounds (33). They were all found to be active, particularly I, which has a growth-inhibiting effect of the same magnitude as that of sulphapyridine. In the tuberculosis tests *in vitro*, the compound also showed activity. Experiments *in vivo* are at present in progress, but since the absorption is rather poor it may be necessary to try to increase it before it can be decided whether the effect of the compound in question has been heigthened also on the tubercle bacillus by the substitution with naphthalene derivatives.

Table.

No	Formula	Name	Melting point
I		2-sulphanil-amido-1,4-naphtho-quinone	226—227°
II		4-sulphanil-amido-tri-phenyl-methane	155—156°
III		N^1-methyl-4-sulphanil-amido-tri-phenyl-methane	199—201°
IV		4-sulphanil-amido-tetra-phenyl-methane	264—265°
V		N^1-methyl-4-sulphanil-amido-tetra-phenyl-methane	267—268°
VI		4,4′-tetrame-thyldiamino-4″-sulphanil-amido-tri-phenyl-methane	261—263°
VII		N^4-triphenyl-methyl-2-sulphanil-amido-pyridine	246—248°

Triphenylmethyl-Substituted Sulphanilamides.

Our other working hypothesis is based on the fact that several vital dyes, particularly certain basic triphenylmethane dyes, have an affinity for the tubercle bacillus (34, 35). Hesse and Meissner have studied this question exhaustively and have described a method of testing the staining properties of these dyes in the peritoneal cavity of mice (34). The reason for this affinity is obscure. The chemical configuration is undoubtedly an important factor, but the fact that the bacterium and the dye have different electric charges is also believed to play some part (35). However, these dyes have not been found to have any definite effect in animals infected with tuberculosis. Meanwhile, it is interesting to note that one triphenylmethane dye, viz. rubrophene (trimethoxy-dioxy-oxo-triphenylmethane), has been stated to have a favourable effect on certain forms of tuberculosis (36, 37).

We have now introduced into various sulphanilamides groups which may be regarded as characteristic of the compounds showing this affinity, in order to find out whether the prerequisites for a better action can be created in this way. The substitutions have been made in such a way that the sulphanilamide derivatives obtained would also fulfil the fundamental conditions for a chemotherapeutic effect.

Of the compounds prepared hitherto, the following N^1-derivatives of sulphanilamide may be listed (see Table): 4-sulphanilamido-triphenylmethane (II), 4-sulphanilamido-tetraphenylmethane (IV), and 4,4′-tetramethyldiamino-4″-sulphanilamido-triphenylmethane (VI). Compounds II, IV and VI are interesting as model substances, compound VI also on account of its similarity to crystal violet, which is a powerful vital stain. Like other sulphanilamides substituted at N^1, these compounds, being acid, form soluble salts with alkali. In order to investigate the significance of the acidity of these compounds in their effect, if any, on the tubercle bacillus, which is electronegative (35), we replaced the hydrogen atom at N^1 with a methyl group in a few cases. As examples may be mentioned N^1-methyl-4-sulphanilamido-triphenylmethane (III) and N^1-methyl-4-sulphanilamido-tetraphenylmethane (V).

Although no immediate effect of the N^4-derivatives of sulphanilamide is to be expected, these compounds are nevertheless interesting, since they may become active following transformation in the organism into compounds with a free amino group. In the present case, a substitution at N^4 might be expected to improve the contact, just as much as a substitution at N^1, after which the sulphanilamide as such can exert its effect, on the condition that fission occurs. The compounds of this kind prepared by us include N^4-triphenylmethylsulphanilamide (m. p. 215—216°) and N^4-triphenylmethyl-2-sulphanilamido-pyridine (VII).

The first stage of the chemical part of these experiments has recently been completed (38). Since the compounds are difficult to dissolve in water and, in addition, are poorly absorbed, we have begun to make them in more soluble form, e. g. ethyl-α-sulphonates and other soluble derivatives.

p-Aminobenzoic Acid in the Tubercle Bacillus.

The effect of the sulphanilamides is neutralized by p-aminobenzoic acid both *in vitro* and *in vivo*. The mechanism of this antagonism is not yet thoroughly understood, but in general it is believed that the sulphanilamides take the place of the p-aminobenzoic acid in a ferment system and that the resultant complex is unable to exercise the functions of the natural ferment. This view of the matter sounds plausible, though its accuracy has yet to be proved. Another explanation, if only complementary, of the mechanism, might be that it is rather the actual synthesis of certain essential substances that is inhibited by the sulphanilamides.

The fundamental condition for the activity of the sulphanilamides against the tubercle bacillus is that this bacterium also requires p-aminobenzoic acid as an essential metabolite. Indirect proof of this is furnished by the observation that the bacteriostatic action of sulphathiazole (39) and promine (40) *in vitro* is inhibited by p-aminobenzoic acid, but no experiments have been conducted directly to demonstrate p-aminobenzoic acid in the tubercle bacillus. We therefore made determina-

tions of this kind, using both a microbiological (41) and a chemical assay method (42). The former method is based upon the growth response of *Acetobacter suboxydans* to p-aminobenzoic acid, in the latter method p-dimethylaminobenzaldehyde is used, giving a coloured compound with the acid. The cakes of bacteria (a virulent human strain) were finely dispersed and washed, after which they were dried by suction as thoroughly as possible. After weighing (about 100 g in each experiment), they were autoclaved with 10 parts of water at 15 pounds pressure for 30 minutes, and the extract was filtered. The remaining bacteria were treated in the same way with 6 N sulphuric acid for one hour, in order to ensure that the conjugate form of the p-aminobenzoic acid was also included in the assay (43). Both extracts were submitted to microbiological analysis, whereupon it was found that the water extract contained the greater part of the p-aminobenzoic acid. For the chemical assays the solutions were extracted intensively with ether, after which the content in the ether solution was determined colorimetrically. With the chemical method about 0,1 γ per g of moist bacteria was found. We consider this to be more accurate than the microbiological test, which may possibly be influenced by other growth substances (44); furthermore, the values in our determinations were higher than with the chemical method.

Meanwhile, the above investigations showed clearly that the tubercle bacillus really does contain p aminobenzoic acid, but the quantity may, of course, vary in different cases. Under the provision that the p-aminobenzoic acid is of functional significance to the bacterium which forms it — and this is highly probable — all these experiments with sulphanilamides and similar substances in experimental tuberculosis are well-grounded. However, the difficulties involved in this work are obvious. They are not only those which have to be faced in all chemotherapy, viz. damaging the bacilli without damaging the tissue cells; in this case we also encounter additional, special obstacles. In the first place these are to be found in the resistant nature of the bacterium itself, secondly in the circumstance that the tubercle is avascular and exhibits quite

early in its development a zone of protective collagenous fibres. In addition, it may be mentioned that the metabolism of these bacteria is very incompletely understood.

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Signs and Causes of Clinical Hyperglobulinemia.

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In clinical protein chemistry, the fundamental work of O. Hammarsten on the precipitation of serum proteins with electrolytes of varying concentrations and their division into albumin and globulin has been of essential value. The Svedberg (1) gave us the possibility of classifying the proteins after their molecular weights with the aid of the ultracentrifuge. It was then found that the division of the proteins according to their precipitation properties was not an artificial system and that the two groups, albumin and globulin, showed marked differences also as regards other and more important characteristics. The work of Tiselius (2) on the electrophoresis of proteins has shown that we are also able to differentiate subfractions among the globulins. These methods thus give an oportunity for a better analysis of selected clinical cases with deranged patterns of serum proteins.

Ultracentrifugation and *electrophoresis* are actually indispensable in the solution of many theoretical questions but these methods are too complicated to be of direct value in clinical routine work. Clinicians have therefore tried to find simple methods for the differentiation of the protein constituents of the blood. The first and simplest of these is the socalled *formol-gel reaction*, accidentally discovered by Gaté and Papacostas. These authors found that certain sera quickly gelify after the addition of a small amount of formaldehyde. It has been shown that this reaction is chiefly dependent on the content of globulin, and Bing has made extensive analyses, showing that there is usually a parallelism between the glo-

bulin content and the rapidity of gelification. There are certain exceptions to this rule, however (Bing (3), Jersild (4)). The present author has recently shown that a low-molecular (dialysable) factor is necessary for rapid gelification. It is probable that a low concentration of this substance is the explanation of cases with high globulin content and negative formol-gel reaction.

Even if none of the other reactions indicating a disturbed protein balance in the serum may compete with the simple formol-gel procedure, the reaction named after its inventor, Takata, may be a valuable complement. Its principle is the precipitation of certain globulin fractions by a solution of mercuric chloride. Two groups of conditions lead to a positive reaction: a lowered albumin or an increased globulin content. This last condition also gives rise to a positive formol-gel reaction (with some exceptions). It is possible to obtain different degrees of positive Takata reaction by the addition of pathological euglobulin to normal serum (5). Such experiments show that the reaction may have a certain quantitative importance.

Another very simple method is Brahmachari's. A drop of blood is allowed to fall into a vessel containing water. If there develops a cloudiness or a white precipitate of *euglobulin* the reaction is positive. I have tried to develop the method by determining the limits of dilution between incipient and complete precipitation in a serum. This was found to vary in different cases (5). The occurrence of euglobulin in large quantities is uncommon. Only a great experience of pathological sera and a correlation of the results obtained with different methods will show the possible value of this method.

In all hospitals in Sweden, a *sedimentation* reaction (S. R.), i. e. a measurement of the velocity with which the red blood corpuscles sink in citrated plasma, is a routine method just as the measurement of the temperature or the determination of the pulse rate. If the S. R. has a very high value this may usually be explained either by an increase in fibrinogen or by an increase in serum globulin. This was first shown by Fåhraeus (6) in 1921. Bing (7) has recently pointed out that

the simplest way to differentiate between a serum S. R. (globulin increase in the serum) or a plasma S. R. (increase in fibrinogen) is to make a formol-gel reaction on the plasma, since increased fibrinogen gives a strong formol-gel reaction.

When the S. R. value is high, a formol-gel reaction on plasma and serum may decide whether the fibrinogen is increased or not (Bing) and also indicate a globulin increase. The Takata reaction may confirm the findings. This is the usual way to

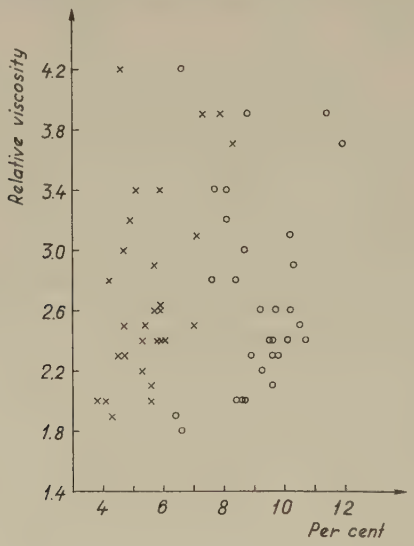

Fig. 1. The relation of viscosity to the globulin (×) and total protein (○) content of the serum in 30 cases with hyperglobulinemia.

decide whether an increase in serum globulin is present before it is estimated by more complicated methods.

All these reactions are very simple but they may still give a characterization of the pathological globulins found in a given case. A determination of total protein e. g. by the method of Bing (8) or the biuret method is also within the scope of an ordinary hospital laboratory.

In order to correlate all the possible characteristics of pathological globulins it is necessary also to make determinations of the protein fractions with the aid of precipitation with electrolytes, electrophoresis and if necessary also by ultracentrifugation. Only such a systematical investigation of all

data for the same patient will make it possible to find a number of characteristics of the protein pattern in different maladies.

Another method that may well become valuable in clinical work on protein chemistry is *viscosimetry* of the serum and plasma. Clinicians seem to have made very little use of the viscosimeter, an instrument that is very simple to handle and still gives information of some importance. The viscosity is obviously often independent of the globulin content in the serum (see Fig. 1). It rather indicates special qualities of the globulin fraction that is present in increased quantities. This fact makes it probable that it will be possible to characterize pathological globulins according to their viscosities. From this point of view, the method is of value as a complement to the formol-gel reaction. Very important also is the determination of the influence of temperature on the viscosity in certain sera. Waldenström (11) has expressed this factor as an index: $\frac{100 \cdot \eta_{13°}}{\eta_{37°}}$. The value at 13° has been chosen instead of 0° or 4° as some sera are completely gelified at these low temperatures. In normal serum the index is 100 but in sera with an abnormal increase in viscosity at low temperatures the index may rise considerably. The results of such determinations on a number of pathological sera will be discussed below. The determinations were performed with a Ostwald viscosimeter submerged in a water bath at constant temperature (thermo-regulator). For the calculation of the relative viscosity (η) the specific gravity of the solution was disregarded, as the variations in this respect between different sera were so small as to be of no importance in the final result.

In order to investigate the behaviour of fibrinogen at different temperatures comparative determinations of plasma and serum viscosity at 13° and 37° were performed. It was found that the plasma viscosity in a large number of instances with high erythrocyte sedimentation might be considerably increased even if the serum viscosity was normal. In other cases both were increased. The temperature index for normal fibrinogen was always low. Only in one case a much higher index was found in the plasma than in the serum (125 and 112 respectively). The fibrinogen in this patient was obviously

Table I.

I. Cases of Hyperglobulinemia with High Temperature Index for Serum Viscosity (≧ 110).

1. *Symptomatical.*

	37°	13°	Index	Glob.%	
O. S.	1.8	2.8	127	4.5	Uremia N. P. N. 360
J. W.	1.8	2.8	127		Arthritis + Endocarditis
E. T.	1.8	2.2	122		Liver cirrhosis
J. L.	1.8	2.2	122		Arthritis?
T. A.	2.4	2.7	112	5.7	Arthritis + Endocarditis
E. B.	2.8	3.4	121	5.1	Tumour
O. K.	2.5	2.8	112	4.9	»
» (plasma)	3.2	4.0	125		»
S.	2.4	—precipitation			Arthritis chron.
E. O.	3.0	4.5	150	7.3	» »
Antidiphtheria serum	2.8	3.2	114		

2. *Essential.*

H.	2.8	3.1	110	7.1	»Ess.»
L.	3.3	3.9	118	7.9	Myeloma Plasma cells increased.
J. W.	2.2	2.6	118	5.9	»Ess.» » » »
O. W.	3.2	3.7	115	8.3	Myeloma » » »
D.	3.0	5.5	173	7.3	» » » »
J. B.	2.7	3.0	111	7.5	» » » »
B. L.	3.2	3.8	118	10.2	» » » »
K. J. J.	5.4	6.5	120	7.8	»Ess.»
E. A. A.	14.0	—30.0	211	10.8	»Ess.»
A. A.	2.5	3.0	120	5.9	Myeloma?
B. G.	2.0	2.4	120		»Ess.?»
J. S.	2.6	2.9	111	5.7	»Ess.»

II. Cases with Slightly Increased Index (100—110).

L. E.	2.6	2.7	104	5.9	Lupus erythematodes
E. K.	2.4	2.6	108	5.9	Liver cirrhosis (atrophy).
S. L.	2.3	2.4	104	6.0	» » + carcinoma?
H. N.	2.4	2.5	104	7.0	» »
E.	2.3	2.4	104		» » ?
G. F.	1.9	2.0	105	5.6	» »
A. L.	2.2	2.4	108		Purpura chron.
B. J.	2.2	2.3	104	4.7	Anaemia pern. sanata + ?
E. E.	2.6	2.8	108	5.8	Myeloma?
S. E.	2.4	2.4	100	5.8	No diagnosis
H. H.	2.3	2.5	108	5.4	Purpura chron.

Table I (cont.).

III. The Influence of Dilution on the Index.

	37°	13°	Index	Glob.	
O. W. undiluted	3.3—	4.0	121	8.3	Myeloma?
» diluted (1:1 NaCl)	1.6—	1.8	112	4.2	
D. Undil.	3.0—	5.5	173	7.3	Myeloma?
dil. (1:1)	1.5—	2.0	133	3.6	
K. J. J. undil.	5.4—	6.5	120	8.7	»Essential»
dil. 1:1	2.2—	3.0	136	4.3	
dil. 1:3	1.6—	1.6	100	2.1	
E. A. A. undil.	14.1—	30.0	211	10.8	»Essential»
dil. 1:1	2.5—	3.1	124	5.4	
dil. 1:3	1.6—	1.7	106	2.7	

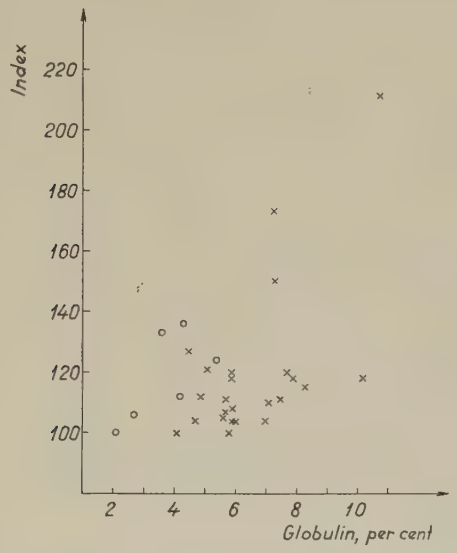

Fig. 2. Globulin content of the serum in its relation to the temperature index for viscosity.

It is seen from the table that among the cases with low index there is only one patient, who probably suffers from myeloma. Her sternal marrow contains numerous plasma cells and the roentgen picture of the skull is highly suspect. On the other hand there is only one case of probable liver cirrhosis in the group with a high index. In spite of this several instances of this disease with low index show high values for serum globulin (6—7 per cent). This is a common finding, that the globulin value per se is not the explanation of a high index (see Fig. 2). I think that the moderate influence of dilution on the index is the best proof of this fact.

pathological in several respects (no firm clot formation after recalcification). The determination of the index may obviously be of value in the study of pathological fibrinogen.

Serial determinations of viscosity at different temperatures with regular intervals give curves of a typical shape and allow the registration of discontinuous changes. Sera in which a precipitation of globulin was found at low temperatures have been investigated by Stein & Wertheimer (9) from dogs and from one patient suffering from kala azar. A patient suffering from chronic polyarthritis with a globulin crystallizing from the serum at low temperatures was investigated by Holmberg and Grönwall (10). Lately Lehmann observed a very striking instance of a similar kind. Some observations made on a serum that showed complete gelification below 7° were published by the present author (11).

In clinical work we are accustomed to find certain regular chemical changes in the blood as signs of different diseases. An increase in blood sugar is the most reliable symptom of diabetes, a low serum iron is always found in iron deficiency anaemia, variations in the uric acid content of the blood are the best diagnostic criteria for gout etc. A systematic analysis of the protein picture in the blood in a great number of conditions ought to give a similar correlation between chemical changes and definite forms of disease.

Before discussing the results that may be obtained with these methods and the possible explanation of hyperglobulinemia, I shall deal briefly with the conditions in which hyperglobulinemia may be found and the nature of the fractions that are increased.

The classical malady for the study of the blood proteins is myelomatosis. This has been the object of intensive study and the results have been ably summarized by Gutmann and coworkers (12). These authors place the cases of myeloma in three groups according to the protein pattern in their blood.

1) Increase in euglobulin or pseudoglobulin I corresponding to an increased γ-globulin. In these cases there is usually little or no Bence Jones protein and the globulin pattern is that seen in chronic infections.

2) Sera with or without hyperglobulinemia, giving a variable pattern due to significant Bence Jones proteinemia.

3) Sera of apparently normal protein composition.

The last-named authors have investigated the sera from 10 cases of myeloma electrophoretically. Kekwick (13) has published 5 such cases, Longsworth, Mc Innes and Shedlovsky (14) 3 cases (published again by Gutmann *et al* (12)). In these 15 instances, an increase was found in the γ fraction in 7. The β-globulin was increased in 5. Two sera were normal. One showed an extra fraction of unknown type but the ordinary Howe fractionation showed a normal picture. It is therefore not permissible to maintain that the serum is normal when only a chemical and no electrophoretical analysis of its protein components has been made.

Chronic hyperglobulinemia is a regular symptom in conditions very different from myeloma. Infection with a virus (Lymphogranuloma venereum), a protozoon, Leishmania (kala azar), a bacillus, Streptococcus viridans (endocarditis lenta) and a worm (schistosomiasis) are instances of maladies that are often accompanied by globulin increase. In rare cases of malaria, lepra and tuberculosis this is also found. Maladies probably of chronic infectious nature such as lymphogranulomasosis benigna (sarcoidosis) and maligna (Hodgkin) and chronic arthritis may also be quoted. It has been shown lately that liver cirrhosis may cause a considerable increase in serum globulins. The etiology of liver cirrhosis remains obscure, but in some of our instances of this disease it does not seem improbable that the primary process was a hepatitis, a disease almost certainly caused by a virus infection.

Among acute maladies pneumonia shows a very marked rise in serum globulin accompanied by hyperinosis. It was shown by Blix (15) at an early stage that this was caused by an increase in α-globulin. This is a very uncommon finding as antibodies have usually been shown to belong to the γ-globulin fraction (Tiselius and Kabat (16), Heidelberger and Pedersen (17) et. al.).

The following table shows the results of some large series of protein analyses on materials from internal clinics.

Table II. Cases with a Globulin Value ≧ 4 %.

Diagnosis Authors:	W. T. W.[1]	J. & S.	S—r	G.M.G.M.K.	Bing	J. W
Myeloma		7	5	21	31	8
L. gran. venereum		1		8		
Tuberculosis (amyloid)	3				8	1
Sarcoid				4	2	2
Acute polyarthritis	2				1	
Chron. »						1
Endocarditis	4			2	6	2
Lupus erythematodes				1		1
Liver cirrhosis			6	7	18	7
Chron. nephritis	2		3			1
Cancer			2			2
Undiagnosed						4
Purpura hyperglob. (11)						2
»Premyeloma						2
Bing-Fog-Neel syndrome (Acta med. scand. *88*, 1936)					3	
Essential hyperglob. (11)						2
Kala azar (20)				1		
Schistosomiasis (21)						
	11	8	16	44	69	35

[1] W. T. W. = Westergren, Theorell and Widström (18) 1931.
J. & S. = Jeghers and Selesnick (19) 1937.
S—r = Snapper (22) 1937.
G. M. G. M. K. = Gutman, Moore, Gutman, Mc Clellan and Kabat (12).
Bing = Bing (3) 1940.
J. W. = present author.

Among my own cases there were also single instances of the following maladies: Hypernephroma, Infiltratio pulm. (tumour?), Hepatitis.

With the exception of the maladies that have just been discussed, it is obvious that the diagnoses are very varied, as single instances of hyperglobulinemia have been found in a great many maladies (e. g. malaria, lepra, »leuchemia» etc.). These instances need hardly be discussed, as it is never certain that the malady itself and not some complication is the cause of the globulin increase. As the infectious diseases obviously play a large part it is tempting to assume that the

formation of antibodies (usually γ-globulins) is the explanation. In other conditions the real cause is unknown and in such cases it is to be hoped that a thorough analysis of the protein pattern may give a better understanding of the disease itself. Some case histories in very abridged form are given below.

Instances of Chronic Hyperglobulinemia, Often of Benign Nature.

Liver Cirrhosis?

Low values for serum albumin have long been known to occur in cirrhosis of the liver. This fact has been used as an argument to indicate the rôle of the liver in the formation of albumin. By most authors the positive TAKATA reaction in this disease is regarded as caused by albumin decrease. In later years the instances of liver cirrhosis with considerable increase in serum globulins have become rather numerous. In none of the cases described *here* was there any anatomical diagnosis, and it is possible that a cirrhotic process is not the real cause.

G. F. Girl born in 1932. In 1940 S. R. 108 mm. Since then very high values. In 1944 slight icterus (index 12). General condition very good. Globulin value 5.6 %.

In this case the increase in S. R. was the first pathological sign. The disease is obviously very chronic but present signs of severe liver damage show that the prognosis is probably bad.

A. Ö. Woman born in 1881. 1931 severe weight loss (22 kg.). S. R. 98 mm/hour. Later MEULENGRACHT 20. TAKATA neg. Formol-gel 90′. Afterwards S. R. of about 100 mm/hour on different occasions. In Febr. 1943 S. R. 110. MEULENGRACHT 14. Albumin 3.6 %, globulin 3.4 %. March 1944 no subjective troubles.

Sarcoidosis (Lymphogranuloma benignum. Schaumann).

G. H. Woman born in 1886. In 1934 bilateral parotitis. Fever. S. R. 124 mm. In 1937 S. R. 110 mm. Ultracentrifugation of the serum showed considerable increase of a globulin fraction with normal molecular weight (K. O. PEDERSEN). Purpura for 10—15 years. Typical picture of lymphogranuloma benignum in a lymph gland. Diagnosis: uveoparotitis. Purpura as before. In 1943 S. R. General condition rather good. The patient may be considered as an instance of purpura hyperglobulinemica (see later),

but is regarded as suffering from sarcoidosis as this disease is known to cause hyperglobulinemia.

E. G. Woman born in 1902. In October 1935 uveoparotitis. S. R. 100 mm. Plasma globulin 5.8 %. In 1942 condition unchanged. S. R. 115 mm. Serum globulin 5.6 %. No subjective troubles.

Purpura Hyperglobulinemica (Waldenström (5)).

The next two cases histories and the history of G. H. have been grouped together as they show a common symptom, namely chronic purpura, and all also suffered from marked hyperglobulinemia. It is difficult to decide the rôle played by the protein derangement in the development of the purpura. Case G. H., who suffers from a disease that is one of the most common causes of chronic globulin increase (sarcoidosis), also shows a purpura of the same chronic type. It is therefore possible that the sarcoidosis is the primary process causing the hyperglobulinemia, as other patients with this symptom but no signs of sarcoidosis also show purpura. It is perhaps permissible to assume that the purpura is a result of the derangement in the serum globulins.

G. H. see sarcoidosis.

H. H. Woman born in 1891. Purpura since 1920. In 1932 chronic purpura S. R. 98 mm. In 1935 S. R. 110. About the same condition in 1936, 1942, 1943 and 1944. In 1943 serum globulin 4.6 %. No more severe subjective troubles.

A. L. Woman born in 1915. Since Sept. 1940 purpura on both legs. In Juni 1942. S. R. 115 mm. In October serum globulins 5.7 %. In Oct. 1943 globulin 3.8 %. S. R. 97 mm. In 1944 106. Feels quite well.

Lupus Erythematodes?

L. E. Woman born in 1900. In 1941 signs of lupus erythematodes? S. R. 120 mm. Subfebrile. In 1943. S. R. [115]. Globulin 5.9 %. In 1944 S. R. 138 Glob. 6.6 %. Signs of arthritis. General condition very good for several years. No signs of myeloma or liver damage.

Cases without Definite Diagnosis.

S. E. Woman born in 1898. In 1937 S. R. 22 mm. In 1940 maximum 75, minimum 39 mm. In 1941 40—50 mm. In 1942 50—60 mm. In 1943 70 mm. In 1944 100 mm. Low standard metabolism but no signs of myxedema. Treated with thyroid

with good results subjectively, but no influence on the serum protein level. Last globulin analysis 1944: 5.1 % (about the same in 1942 and 1943). No signs of myeloma. No purpura. No signs of liver damage. Very good general condition. Increased S. R. for at least 4 years. No tendency to improve.

A. P. Woman born in 1868. In 1940 gastric troubles. Lost weight (10 kg). S. R. 110 mm., otherwise nothing definitely pathological. In 1942 red spots on both legs most closely resembling a thrombophlebitis. S. R. as before. The cutaneous symptoms soon disappeared. In 1943 still the same high S. R. Globulin 4.3 %. In 1944 S. R. 95 mm. No signs of myeloma, no purpura, no signs of liver damage. General condition rather good, in spite of very high S. R. (hyperglobulinemia) for 4 years.

Premyeloma?

J. W. Woman born in 1878. In 1938 swelling of the left wrist. In 1941 S. R. 116 mm. very low body weight (37 kg). The S. R. was constant at about 100, also in 1942 and 1943. Globulin 6.1 %. In 1942 and later sternal marrow: plasma cell proliferation. On Röntgen diffuse osteoporosis, no myeloma. The case was regarded as a possible instance of »premyeloma». Her general condition was rather poor. No pains. She died from a lobar pneumonia in 1944. The Post-mortem showed numerous plasma cells in the bone marrow but no foci resembling myeloma. The diagnosis thus remains uncertain. It seems possible that the patient might have developed a myeloma later if she had not died from pneumonia. Another explanation would be that the increase in plasma cells was purely reactive against some unknown agent.

In recent years there have been published a number of cases resembling myeloma but not showing all the symptoms necessary for a definite diagnosis. The chief difference between classical myeloma and what is now diagnosed as diffuse myelomatosis invading the whole bone marrow and accompanied by maximal hyperproteinemia, is the localized, nodular arrangement of myelomatous tissue. Whether this is sufficient to allow a distinction is not easy to tell. Many authors agree nowadays that a purely histological differentiation between reactive plasma cells and myeloma cells may be impossible. Gormsen (23), who has made a recent very extensive study of this problem, has shown with exact measurements that the nucleus is often definitely bigger in myeloma cells than in normal plasma cells. Instances are found, however, of typical myeloma where all cells have a normal nuclear size. The nucleoli are often larger and more irregular (Zadek, Gormsen) but cases are also met with where the cells are

absolutely identical with normal plasma cells also in this respect. Gormsen (23) writes in conclusion. "Even if it is possible in most cases to make a certain diagnoses, there are however found instances, where it is impossible to differentiate a myeloma from a reactive increase in plasma cells". The incidence of cells with two nuclei or of mitosis is no greater in myeloma cells than among normal plasma cells from the bone marrow.

My experience of sternal punctures from 14 cases of myeloma is quite identical with Gormsen's and it is often difficult to distinguish a marrow with plasma cells in a case with other typical signs of myeloma from the cells found in other conditions. Rohr also stresses the point that the bone narrow in lymphogranuloma venereum and also in a case of pneumonia (illustrated by a very beautiful coloured plate) may be confused with a myeloma. In kala azar the bone marrow is also said to be very similar to a myeloma.

There is thus an unbroken series of cases with similar bone marrow changes from the so-called symptomatic reactive increase in plasma cells via the diffuse myelomatosis, which may quite well be a reaction to some unknown noxa, to the classical myeloma which has always been regarded as a true tumour. I have pointed out in a previous paper (24) that many clinical features in this malady do not fit in well with its alleged nature as a malignant neoplasma. The absence of metastases and of a primary tumour and the marked derangement of protein metabolism are such features.

One of the most striking features of all these case histories is the extreme chronicity of the hyperglobulinemia. It seems tempting to ask whether these conditions are not really incurable and whether the tendency to formation of a pathological or at least a pathologically increased globulin fraction is not a life-long disorder of protein metabolism. As a matter of fact none of the patients with unexplained hyperglobulinemia seems to have recovered from this disturbance during a long period of observation. Among my own 31 cases with globulin > 4 % there are 13 who have died, 7 who were recently discovered, 8 very chronic cases but only two who were cured of their malady (acute hepatitis and probable endocarditis). This may be explained in several ways. We know from the foregoing that a globulin increase is usually reactive, for example against an infection. After inoculation of rabbits with polyvalent strains of pneumococci a very considerable rise

in globulin is found, even at the expense of the albumin (Björneboe (25)) and the work of later years has shown that this is chiefly of the γ-type. Practically all the globulin is present in the form of antibody and is therefore specifically precipitable. After cessation of the antigen administration the globulin increase usually diminishes and gives way to normal values.

If the globulin increase in my cases be regarded as a reaction to some foreign process e. g. an infection, it seems necessary to assume that this is of an eminently chronic nature.

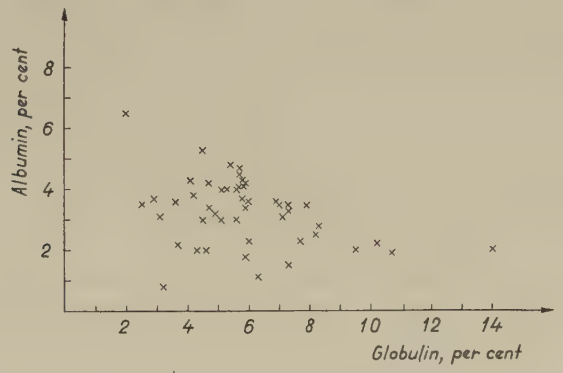

Fig. 3. Relation of serum albumin to serum globulin in 45 cases of hyperglobulinemia.

In one group of patients suffering from essential hyperglobulinemia there was present a globulin fraction with peculiar properties. These were investigated by K. O. Pedersen at the Institute of Physical Chemistry University of Uppsala. He found that the value for the sedimentation constant indicated a molecular weight of about one million. In its electrophoretic properties it most closely resembled a β_2-globulin. The many peculiar characteristics of these substances were discussed in a paper by the present author (11). The values for serum albumin were very low when determined both by salt precipitation and by electrophoresis (see Fig. 3). Not only the albumin, but also the third protein component of the blood plasma, the fibrinogen, was sometimes very much lowered. To explain this I have advanced the hypothesis that the foreign globulin found in these cases was really to be compared with

a virus protein, and the normal globulin be formed after this pattern. It seems probable that only one fraction is increased in hyperglobulinemia and never the globulin as a whole. It is possible that some of the maladies described in this paper, where there is no tendency to regression, are really instances of chronic virus infection. When an opportunity arises to infect monkeys this problem will be tested experimentally. At present it is not possible to decide whether the special globulin fraction really is virus protein itself or whether it is to be regarded as an antibody.

Many problems in hyperglobulinemia are still unsolved and only a beginning has been made in their investigation. Progress will only be possible if there is cooperation. The clinicians, who are able to select and classify the cases, study the influence of certain factors (e. g. blood and plasma transfusions with plasmapheresis) and determine simpler characteristics by formol-gel, Takata, S. R., euglobulin, biuret reaction, viscosimetric and possibly dilatometric methods. The chemists and physico-chemists study e. g. the electrophoretic properties, the ultracentrifugal characteristics, and such qualities as birefringence etc. It is to be hoped that this work will not only lead to a better classification of obscure disease processes but also to a deeper understanding of the factors governing protein synthesis and protein destruction.

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Some Comments on the Large Scale Production of Transfusion Plasma.

By Gösta Widström.

The Swedish Military Board of Health.

In the year 1939 the Institute of Physical Chemistry, University of Uppsala, was commissioned to test and work out methods for the processing and drying of human plasma. Professor Tiselius and the present author were entrusted with this task. At that time a great deal of work had already been done on these problems in U. S. A. and Great Britain, and the literature was abundant. After an interval during which hardly any Anglo-Saxon literature has been available in this country, publications from U. S. A. and England are again coming in. It is therefore of a certain interest to note that the practical experience in this field abroad corresponds fairly closely to our own.

There is still a great variety of methods. Differences are due to differences in scale, other local circumstances and a certain conservatism. The small scale production of plasma will hardly be uniform in method, but the large scale production shows a tendency to standardisation. It will, however, obviously take some time before this is fully attained. At the present juncture it is therefore still of value to compare different solutions of the problem. A short account will be given here of how defibrinated plasma is produced to meet the requirements of the Swedish army according to methods that originally were worked out in the Uppsala laboratory.

The blood is collected in blood banks in 400 ml bottles, sterilized with 40 ml 3.8 per cent Na citrate + 2 ml 20 per cent Na sulphathiazole. The bottles are kept in refrigerators.

They are transported in insulated cardboard boxes, preferably during the cooler part of the day.

As a rule 3 or 4 days after the collection, preferably not later, the blood is mixed in about 10-litre portions which then contain blood from all groups in approximately the same proportions as the natural distribution of blood groups. In this way complete neutralization of iso-haemagglutinins is obtained The mixed blood is passed through gauze and is separated in a DE LAVAL blood separator at a rate of about 15 litres per hour. The yield is about 60 per cent citrated plasma, which is obtained almost clear and without haemolysis, but the plasma still contains about 0.01 per cent red blood corpuscles. If the plasma is once more passed through a separator, in this case used as a clarifier, the plasma is obtained as an almost clear solution with no admixture of blood cells. This clarification considerably facilitates the final filtration, which is thus made more rapid. Moreover, a larger amount of plasma can now be passed through each set of filters before they become clogged.

After the separation of the plasma it is recalcified with a calculated amount of $CaCl_2$ solution. The fibrin is separated off either by vigorous shaking in glass bottles in portions of 5—10 litres or by stirring larger portions in containers of stainless steel with a whisk of the same material. In both cases the fibrin is separated as firm threads in a form resembling cotton waste, and without any appreciable loss of plasma.

After defibrination of the plasma it is frozen in containers of stainless steel and kept at a temperature of —20° C. After storing for various periods the plasma is thawed out, passed through a SEITZ filter and is either dried or distributed as fluid plasma. The above-mentioned freezing process preserves the plasma for a considerable time. One thus also obtains an easily available supply for further processing. It would also appear that the fluid plasma that has been subjected to this treatment remains clear for a longer time when stored in a cooling room than plasma that has not been pre-frozen. This pre-freezing has probably had the effect of forcing out a certain amount of unstable matter.

A principle that has been observed throughout in our plasma production is that neither the blood nor the plasma is allowed to approach room temperature for longer periods than absolutely necessary, and that the periods when the plasma is not in the frozen state or has been passed through a sterilization filter or dried are as short as possible. The period beginning with the collection of the blood and ending with the final product does not exceed 6—7 days, excluding the period when it is kept in the frozen state.

In order further to diminish the risk of deterioration of the plasma, we have considered it desirable to add a bacteriostatic. After having tested a good many of the generally proposed preservatives on a small scale, we finally chose Na sulphathiazole in a concentration of 0.1 per cent. We found it most logical to add it together with the anti-coagulant.

All preparative work is carried out with all due precautions of sterility and asepsis, but entails operations, in the first place the use of separators, that render contamination from the air inevitable. Sterility tests were carried out on a series of samples taken from 10-litre portions of plasma after defibrination (a stage in the process when the risk of bacterial contamination is greatest) and afterwards allowed to stand for 10 days at room temperature. Fewer than 5 per cent were found to be infected. The processing of transfusion plasma gives this contamination no chance to multiply, and the results of the above tests are a good demonstration of the value of sulphathiazole as a preservative.

Only a few words will be devoted to the drying of the plasma. In 1939 a medium-sized chryochem apparatus with a drying capacity of about 3 litres was built in Uppsala. In this were dried about 70 doses of 400 ml plasma. The product was very readily soluble, and gave a clear solution. Ultracentrifugal and cataphoretic diagrams and the results of transfusion tests were as for undried plasma. Our own experience of this method has thus proved to be as satisfactory as that of other authors. At about the same time, *Kärnbolaget* in Stockholm worked out a method for drying susceptible biological material on a large scale, (the Transin method). In an apparatus constructed to dry 200—300 litres of plasma per

day, one obtains dried plasma as a fine powder, which is distributed in bottles in amounts corresponding to 350 ml of plasma. The powder is readily soluble in distilled water, giving a clear solution. Ultracentrifugal diagrams and the results of transfusion tests were identical with those for undried plasma.

Summary.

A description is given of the method used for the preparation of transfusion plasma for military purposes in Sweden.

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Om *Carex macloviana* d'Urv. och dess utbredning i Nordeuropa.

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1. Historik.

Redan i första upplagan av C. J. Hartmans Handbok i Skandinaviens flora, utgiven år 1820 beskrives denna art men blott såsom varieteten β *ovata* under *Carex leporina* L. Beskrivningen är ytterst kortfattad: »axet tätt äggrundt.» Om utbredningen lämnas inga närmare upplysningar än att varieteten är »Fjv.» (= fjällväxt). Andra upplagan av samma flora (år 1832) är utförligare: »β Fjellv. Lul. Lpm. Jtl. — — — liknar mycket *C. lagopina*, för hvilken författ. emottagit den fordom af Prof. Wg.» (Göran Wahlenberg). Tyvärr nämnes ingenting om dessa Wahlenbergska exemplar äro det material, på vilka Hartman ursprungligen beskrivit sin var. *ovata*, men detta är mycket sannolikt, då Wahlenberg före 1820 företog flera resor i Lappmarkerna, medan Hartman själv icke varit nordligare än i Jämtland och angränsande delar av Norge under sin botaniska resa år 1813. »Jtl.» (= Jämtland) torde kunna betraktas som ett tryckfel. I tredje upplagan (år 1838) upprepas samma korta beskrivning samt »β i fjellen.» Anledningen till den mindre än tidigare preciserade uppgiften om utbredningen ligger sannolikt däri, att Hartman trodde, att var. *ovata* var relativt vanlig i fjälltrakterna. Vid denna tid framfördes också teorier om växternas »föränderlighet» och att en mängd arter med stor utbredning på den skandinaviska halvön ersattes norrut och särskilt i fjälltrakterna av i vissa hänseenden avvikande former, som emellertid tillmättes ringa systematiskt värde. I detta sammanhang bör framdragas en

hittills knappast beaktad notis om *Carex macloviana* i L. L. Laestadius avhandling »Loca parallela», som enligt författarens underskrift förelåg färdig redan år 1831 men blev tryckt först år 1839 i Nova Acta Regiae Societatis Scientiarum Upsaliensis, vol. XI. Laestadius framhåller (l. c. p. 222), att gräsartade växter i fjällen få kortare strå samt färre och större blommor och anför härpå en rad exempel, bl. a. just *Carex macloviana* men under namnet *Carex leporina* var. *subalpina*. I en not (l. c. p. 223) skriver han: »Spiculis in spicam congestis, (num *C. ovalis* Good.) rufo-fuscis; capsulis concavo-convexis, margine serrulatis, squamis longioribus. Legi ad Quickjock et Peurajaas [tryckfel för Peurajaur = Peuraure, en gård vid sjön med samma namn sydöst om Kvikkjokks kyrka] 1821.» Laestadius' förmodan, att hans var. *subalpina* kunde vara identisk med den av Goodenough beskrivna *Carex ovalis* är felaktig, då den sistnämnda är detsamma som *C. leporina*, d. v. s. huvudarten.

Hittills torde endast obetydligt och sannolikt även illa preparerat herbariematerial stått de nordiska botanisterna till buds för undersökning. Först sedan Elias Fries i den år 1842 utgivna åttonde fascikeln av exsickatverket Herbarium Normale såsom nr 82 utdelat goda exemplar av denna växt, blev det möjligt att mera vetenskapligt undersöka densamma. Fries inför nu namnet *Carex festiva* Dewey och placerar å de tryckta etiketterna såsom synonymer *C. leporina* var. *ovata* Hn och *C. leporina* var. Laest. Professorn i botanik i Kristiania M. N. Blytt företog år 1841 en resa i Nordnorge och samlade denna växt på fjället Tromsdalstind nära Tromsö. Han lämnade Fries ett tillräckligt antal exemplar för utdelning i exsickatet. *Carex festiva* beskrevs år 1836 av C. Dewey, professor vid Rochester University, i The American Journal of Science and Arts conducted by Benjamin Silliman [därför oftast citerad »Silliman's Journal»], vol. 29, tryckt i New Hayen Conn., 1836. Då uppsatsen är svåråtkomlig, återges här Dewey's beskrivning (l. c. p. 246) in extenso:

»No. 147. *C. festiva*, D. Tab. W. fig. 71. Spicis distigmaticis androgynis, superne pistilliferis subsenis ovatis in capitulum densi aggregatis; fructibus ovatis oblongis rostratis in apice serrulatis bifidis convexo-planis, squama ovata acutiuscula longioribus.

Culm six to ten inches high, scabrous, triquetrous, striate, erect, stiff, leafy; lower leaves shorter, upper ones longer than the culm, flat, striate, rough on the edge; spikelets about six, androgynous, staminate below, ovate, aggregated into a close head, without bracts; stigmas two; fruit ovate, sub-oblong, compressed, convex above, nearly flat below, acuminate, rostrate, split at the mouth and scabrous on the edge; pistillate scales ovate; acutish, tawny, shorter than the fruit; color of plant light green.

Found by Dr. Richardson at Bear Lake and on the Rocky Mountains.»

Namnet *Carex festiva* Dew. användes sedan av Hartman i samtliga upplagor av Handbok i Skandinaviens flora från och med den fjärde, som utkom år 1843, för den nordskandinaviska varieteten av *Carex leporina*, och andra utgivare av liknande arbeten över nordens flora behöllo detta namn till långt in på 1920-talet. Hartmans beskrivning i fjärde uppl. hänvisar till Herbarium Normale, fasc. 8, n:r 82 och slutar på följande sätt: »Mycket lik föreg. [= *C. leporina*] och knappt skiljd med annat än det dubbelt kortare, men tjockare axet, mörkt af de svartbruna hinnkantade fjällen. — C. lepor. β ovata Handb. ed. 3.»

Här må inflickas, att det är svårförklarligt, varför K. K. Mackenzie i North American Flora, vol. 18 (1931), p. 127, skriver: »Note: *C. leporina* var. *ovata* Laest. is referable to *C. leporina*, and not to this species.» (= *C. macloviana*). Att Laestadius i st. f. Hartman uppges vara namngivare, beror sannolikt därpå, att G. Kükenthal (i Engler's Pflanzenreich, IV:20 [1909], p. 195) för *C. macloviana* såsom synonym anför »*C. leporina* β *ovata* Laest. in Hartm. Handb. ed. 3 (1838), 216». Kükenthal torde i sin tur hämtat det felaktiga citatet från N. J. Andersson som i Cyperaceae Scandinaviae (1849), p. 63 har som synonym för *Carex festiva* Dewey medtagit »*C. leporina* β *ovata* (Laest.) Hn», trots att Laestadius för denna växt aldrig använt annat namn än var. *subalpina*.

Från och med fjärde upplagan av Hartmans flora äro utbredningsuppgifterna i huvudsak lika. Ed. 4: Torne Lpm, Lule Lpm och Finnmarken (= Västfinnmarken, d. v. s. Troms fylke). Ed. 5 t. o. m. ed. 10: Torne—Ume Lpm, Finnmarken. I ed. 11 (år 1879) tillkommer Vb [= Nb], Kengis, medan utbredningen i Norge ändras till Tromsö amt; Tromsdalstind och Nordland:

Ranen. Ett par i ed. 5 och ed. 6, resp. ed. 5— ed. 10, efter Lindeberg och Lindblom citerade fynd från Sogn och Romsdalen ha strukits i ed. 11, då dessa uppgifter enligt vad Blytt meddelat redan år 1861 i Norges flora, I, p. 197 med all sannolikhet gälla andra former av *Carex leporina*.

Genom G. Kükenthals förut citerade *Carex*-monografi blev det allmänt känt att redan år 1826, d. v. s. tio år tidigare än Deweys beskrivning över *C. festiva* publicerades, hade samma växt beskrivits från Falklandsöarna under namnet *C. macloviana*. Första gången detta namn förekommer i svensk botanisk litteratur är i Otto R. Holmbergs referat av nämnda monografi i Botaniska Notiser för år 1909, p. 314: »*C. macloviana* d'Urv. in Mém. Soc. Linn. Paris. (1826) = *C. festiva* Dew. (1836).» Holmberg använder också namnet *C. macloviana* d'Urv. i en av honom för Lunds Botaniska Förening sammanställd »Förteckning över Skandinaviens växter», utgiven år 1917. Det dröjde emellertid ända till år 1926, att C. A. M. Lindman ansåg det berättigat att följa nomenklaturreglerna och sätta *C. festiva* som synonym till *C. macloviana* i andra upplagan av Svensk fanerogamflora. I den år 1918 tryckta första upplagan placerar han med frågetecken *C. macloviana* såsom synonym efter *C. festiva*.

Carex macloviana beskrevs, såsom förut omnämnts, från Falklandsöarna av Jules-Sébastien-César Dumont d'Urville. Denne var sjöofficer och naturforskare, särskilt botanist och entomolog, och deltog i Duperrey's antarktiska expedition med fartyget Coquille 1822—1825. Då beskrivningen även av *Carex macloviana* är publicerad i en svåråtkomlig tidskrift (Mémoirs de la Société Linnéenne de Paris, tome 4, 1826, p. 599), återgives här originaldiagnosen:

»8. *C. macloviana*. Spiculis 7—9 androgynis infernè masculis densè congestis, basi bractea aristata suffultis. Stigmatibus binis. Squamis fulvis acutis dorso minutissimè scabris. Culmo triquetro foliis gramineis breviore.

Culmus 3—5 pollicaris, spica vix 8-linearis. Folia glabra canaliculata. In apricis crescit. 4 (3) (3).» (Siffrorna betyda, att denna art förekommer på ett område motsvarande 3 % av den undersökta öns hela areal och att den på en viss lokal utgör 3 % av dennas vegetation.)

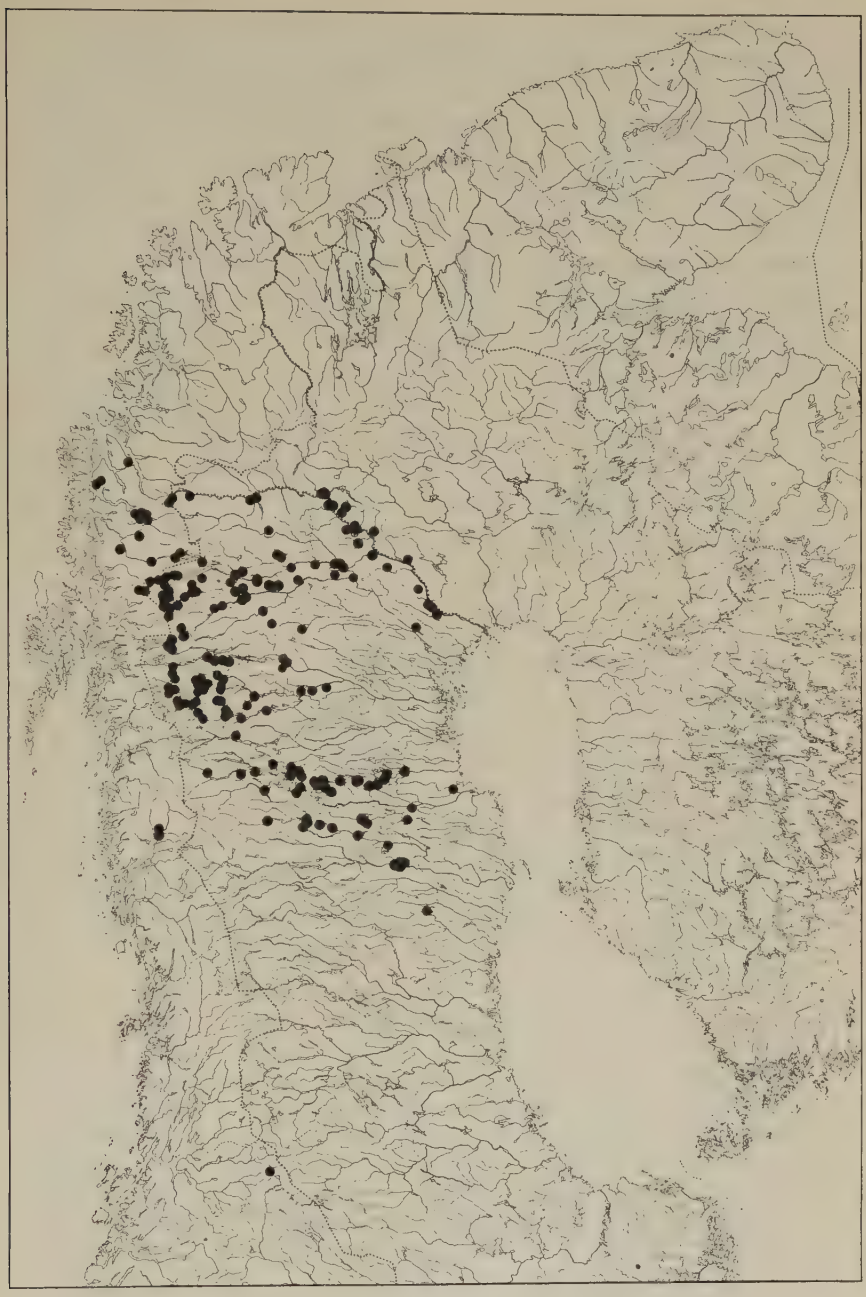
Växten är uppkallad efter Insulae Maclovianae, det latinska namnet på den ögrupp, som på engelska heta Falkland Islands och på franska Les Malouines. Uppsatsen bär också titeln »Flore des Malouines». Någon närmare uppgift om fyndorterna saknas.

Det bör framhållas, att *Carex macloviana* från skilda delar av världen beskrivits under en rad olika namn, t. ex. *C. propinqua* Nees et Meyer (1834) och *C. allomacros* Steudel (1855) från Chile samt *C. inciso-dentata* Steudel (1855) från Magellans sund. Om dessa äro fullt identiska med *C. macloviana* torde ännu icke vara fullt klarlagt. I fråga om den nordeuropeiska växtens identifiering med den som beskrivits från Falklandsöarna är kanske ännu icke sista ordet sagt. Nutida forskare ha stor benägenhet att uppdela en »stor» art med vidsträckt men icke sammanhängande utbredning på mindre utan att lägga vikt vid, om morfologiska olikheter berättiga till en sådan uppdelning med resultat, att vad som lämpligen kunde kallas geografiska raser föres till högre systematiska enheter, som icke kunna bestämmas utan kännedom om härkomsten.

2. Totalutbredning.

Olika forskares uppgifter om totalutbredningen för *Carex macloviana* äro allt annat än överensstämmande, beroende på om vederbörande har ett mera vidsträckt eller mera snävt artbegrepp. Låter man *Carex macloviana* få karaktär av en »storart», innefattande även det 20-tal småarter, varieteter och geografiska raser, som den amerikanske caricologen K. K. Mackenzie uppfört såsom arter inom en grupp kallad *Festivae* i det förut citerade arbetet över Nordamerikas *Caricoideae*, får den en mycket stor utbredning. Denna omfattar nordvästra Europa, d. v. s. Sverige, Norge och Finland samt Island, Grönland och arktiska Nordamerika från Labrador och Gaspé-halvön till Alaska, västra Nordamerikas höga bergskedjor, Mexico (vulkanen Orizaba), Sydamerika från Ecuador och Bolivia, utmed Anderna till Patagonien och Eldslandet, Falklandsöarna, Hawaii samt av Asien de nordligaste Kurilerna och Kamtschatka.

Följer man däremot Mackenzie's mycket snäva artbegrepp,



Utbredningen av *Carex macloviana* inom Fennoskandia.

inskränkes utbredningen för *Carex macloviana* s. str. till Nordvästeuropa, Grönland och arktiska Nordamerika västerut till Mackenzie River och till södra Sydamerika med Falklandsöarna. Däremot skulle alla förekomster i Alaska och Rocky Mountains (varifrån dock *Carex festiva*, som Mackenzie upptager såsom synonym till sin *C. macloviana*, beskrivits av Dewey!) fördelas på andra »arter». Den mest spridda av dessa torde vara *C. pachystachya* Cham. Till denna föra ryska författare de former som äro kända från Kamtschatka (och Kurilerna?). Jag har emellertid från Colorado sett herbarieexemplar, som föga avvika från typisk *C. macloviana*, men som av amerikanska specialister benämnts *C. subfusca* W. Boott (= *C. macloviana* var. *subfusca* [W. Boott] Kükenth.) Denna sistnämnda har ansetts vara identisk med den växt, som sedan lång tid tillbaka är känd från Hawaii. Skottsberg (41, p. 329) har emellertid här samlat tämligen typisk *C. macloviana*.

3. Utbredning i nordvästra Europa.

De å kartan utmärkta lokalerna för *Carex macloviana* i Fennoskandia hänföra sig dels till herbariematerial i Naturhistoriska Riksmuseum, Botaniska avdelningen, Stockholm (R), universitetens botaniska museer i Lund (L) och Uppsala (U) samt i Oslo (O), dels till litteraturuppgifter. Då flera insamlingar gjorts eller omnämnande av fynd skett från en och samma lokal, uppräknas här i regel endast första och sista. I fråga om publicerade fynd utan uppgift om när detta gjorts, angives tryckåret för uppsatsen i fråga. Siffror efter citat hänvisa till litteraturförteckningen.

Sverige.

VÄSTERBOTTEN.

Skellefteå: Varuträsk, gräsmark, 1942, G. R. Cedergren (R). — **Norsjö:** Norsjö by, vägkant mot sjön, 1940, G. R. Cedergren (R). — Bjursele, gräsmark, 1940, G. R. Cedergren (R, U). — **Malå:** Malåsund, slåtterängsbacke, 1924, E. G. Vretlind (R). »Vanlig på tunen och lägdorna i Malå». E. G. Vretlind (1, p. 83 & 90). — **Jörn:** Myrheden, torr gräsmark vid gästgivargården, 1940, G. R. Cedergren (R).

ÅSELE LAPPMARK.

Fredrika: [kyrkbyn], 1909, Th. Wolf (R).

LYCKSELE LAPPMARK.

Lycksele: kyrkbyn, 1853, J. Ångström (R, U); 1938, E. Asplund (R). — Hede, 5 km SSO om Lycksele, 1919, C. Th. Mörner (2, p. 33). — Mindre sandslätt mellan Lycksele—Hvila-landsvägen och Umeälven, omkring 1/2 mil nedom (SSO) Lycksele, 1927, G. Fridner (R). — Nedre Kvarnmyran, 1888, P. F. Lundqvist (U). — »Flerestädes kring Lycksele, mest å gamla gräsvallar, dikeskanter o. s. v.» 1906, N. Sylvén (3, p. [140]). — »Gamm-platsen», 1927, S. Nordenstam (R). — Stenhamn, gräsmark vid landsvägen, 1938, E. Asplund (L, R). — Ruskträsk, 1935, C. Th. Mörner (4, p. 258). — Vindelgransele, 1931, S. Nordenstam (R). — **Tärna:** [kyrkbyn], 1874, N. L. Andersson (U). — **Sorsele:** kyrkplatsen, 1845, N. J. Andersson (5, p. 6). — Pansborg, 1921, D. Gaunitz (U). — Ön vid kyrkan, 1939, G. R. Cedergren (L, R, U). — Nyodlingen, allmän, 1924, D. & C. B. Gaunitz (6, p. 133). — Abmoberg, Antes Lägda, 1924, D. & C. B. Gaunitz (6, p. 133). — Gargnäs by, 1939, D. Gaunitz (7, p. 80). — Sandbäcksflyttjet, W om Storvindeln, 1939, D. Gaunitz (7, p. 80). — **Stensele:** Rastplats vid vägen mellan Barsele och Gunnarn, 1941, L. Wahlberg (40, p. 105).

NORRBOTTEN.

Överkalix: Bränna, 1917, C. Th. Mörner (2, p. 34). — Ohtanajärvi, 1917, C. Th. Mörner (R). — **Övertorneå:** Niemis, 1892, A. N. Lundström (U). — Mellan Ruskola och Alkullen, 5,8 km S Matarengi kyrkby på f. d. gårdsplan och torr äng mellan landsvägen och järnvägen, 1940, O. Lönnqvist (L, R). — Ruskola, på gammal och torr äng ovanför gamla landsvägen 3 km S Matarengi, 1940, O. Lönnqvist (R). — 1,5 km S Matarengi, på torr äng omedelbart ovanför gamla landsvägen, 1940, O. Lönnqvist (R). — Matarengi kyrkby, gräsmatta på gårdsplan, 1940, O. Lönnqvist (R). — Matarengi, 1924, A. Frisendahl & K. Bökman (R, U). — Kuusijärvi, 1902, J. A. Z. Brundin (11, p. 110). — **Pajala:** Sattajärvi, 1902, J. A. Z. Brundin (11, p. 110). — Kengis, 1838, L. L. Laestadius (R, U); 1928, O. R. Holmberg (L. U). — Pajala kyrkby, 1859, C. P. Laestadius (R, U); 1906, F. E. A. Block (L, U). — Lovikka, 1928, O. R. Holmberg (L, U). — »På lergrund efter landsvägen mellan Junosuando och Lovikka gästgifverier», 1890, H. Samzelius (9, p. 176). — Palokorva, 1928, O. R. Holmberg (L, U). — Junosuando, 1923, C. Th. Mörner (10, p. 134). — Kaunisvaara, 1918, J. Montell (U). — Kihlanki, in colle graminoso, 1918, J. Montell (R). — »Ytterligt allmän på ängar och vid vägkanter i Kengis och Pajala», 1902, S. Birger (11, p. 110). — **Muonionalusta:** kyrkbyn, 1904, S. Birger (11, p. 110). — Ön nedom Muonionalusta [kyrkby], 1909, A. T. Hwass (R).

PITE LAPPMARK.

Arvidsjaur: Siksjön, 1917, C. Th. Mörner (2, p. 33). — Abborrträsk, 1883, K. B. J. Forssell (U); 1917, C. Th. Mörner (R, U). — Kalvträsk, 1917, C. Th. Mörner (2, p. 33). — Kyrkbyn, 1909, S. Birger (13, p. 266); Arvidsjaurs kyrkstad, 1934, G. Wistrand (12, p. 20). — Utmed landsvägskanten vid prästbostället, 1918, H. E. Johansson (R). — Baktåive, 1934, G. Wistrand (12, p. 20). — Långträsk, 1909, S. Birger (13, p. 266). — Norrmalm, 1934, G. Wistrand (12, p. 20). — Avaviken, 1918, H. E. Johansson (14, p. 486). — **Arjeplog:** Mellan Baktåive och Allejaur, 1934, G. Wistrand (12, p. 20). — Kasker vid Skellefte elf, 1856, Fr. Björnström (R, U). — Mullholm i Uddjaur, 1874, V. F. Holm (U). — Långvik vid Storavan, 1879, C. Melander (U). — Kyrkbyn, 1873, V. F. Holm (L); vid kyrkan, 1933, M. Engstedt (R). — Prästgården, gräsmatta, 1927, C. G. Alm (L, R, U). — Äng W om kyrkstaden, 1934, G. Wistrand (R). — Galtispuouda, i skogen på västsidan på gångstig, 1936, G. Wistrand (R). — Mellan Stensund och Galtisjaure, 1934, G. Wistrand (12, p. 20). — Radnejaure [= Radnaure], i vall, 1938, G. Wistrand (R). — Dellaure, 1934, G. Wistrand (12, p. 20). — Mellan Båtsjaure och Laisvall, 1943, Th. Arwidsson (35, p. 170). — Högheden, 1943, Th. Arwidsson (35, p. 170). — Jäkkvik, nedanför Peljekaise, 1846, N. J. Andersson (5, p. 9). — Vuoggatjålme fjällstuga, 1932, Th. Arwidsson (35, p. 170). — Märsa, slåtteräng nära gården, 1927, C. G. Alm (L, R, U). — Västerfjäll, 1928, N. Johnsson, (U). — Nurrholm, på västra sidan av Uddjaur, 1874, V. F. Holm (U).

LULE LAPPMARK.

Jokkmokk: Kyrkvallen, 1892, N. E. Svedelius (R); kyrkbyn, 1942, Asta Lundh (L). — Kyrkstaden, 1903, Th. Wolf (R, U); 1936, J. A. Nannfeldt (U). — Söder om Jokkmokks by, 1924, Th. Arwidsson (R). — Randijaure by, 1936, J. A. Nannfeldt (R, U). — Koskats, 1916, C. Th. Mörner (2, p. 33). — Kaddåive [»I fuktig jordmån vid fj^{s} Kedovis fot»], 1879, T. Alm (L). — Peuraure [»juxta Peurajaur»], 1821, L. L. Laestadius (R); 1926, C. G. Alm (R, U); — 2 km NW om »norra gården», 1927, C. G. Alm (L, R, U). — Tjåmotis, 1907, N. Kr. Berlin (L, R); 1916, — C. Th. Mörner (2, p. 33). — Niavve, 1900, J. & A. Frisendahl (L, R, U). — Kvikkjokk, kyrkbyn, 1821, L. L. Laestadius (15, p. 223); torräng i byn, 1942, Sten Selander (R). — Vid turiststationen, 1940, J. Lagerkranz (R). — Vid Kamajokks utlopp, 1923, St. Grapengiesser (R). — Vid Tarrajokk, 1856, E. C. J. Cederstråhle (R, U). — Tarradalen, Kåtnjunjes, torräng vid gångstigen, 1942, S. Selander (R). — Luoppalvaratj, Ranunculus acrisäng i gråvidet, 1943, S. Selander & N. Dahlbeck (R, U). — Kutjaure, nordväststranden, gräsmark i strandkanten, 1928, G. Björk-

man (R, U). — Vid Seperjokks utlopp i Kutjaure, nordsidan, 1939, G. Björkman (16, p. 41). — Vid Vuojatätnos mynning, 1910, G. Jönsson [Ilien] (17, p. 120), — Rapadalen, nedom Stuorra Skårkas, 1902, H. W. Arnell (U). — Låddepakte, 1916, T. Å. Tengwall (R, U). — Matåive, 1915, T. Å. Tengwall (U). — Pårek, 1914, T. Å. Tengwall (L, R, U). — Pårektjåkko; Snavvajokk; Alkatjåkko; Jokotjkaskatjåcko; Telma; Vassjatjåkko; Råtnik; öster om Spatnek; Pelloreppe; Sarvestjåkko; öster om Sarvesjokks mynning; Unna Jerta; Alkavare; Herrapakte; Stuor Rissavare; Virihaure vid Vuojatätno; Låtatj; Skuolla; 1925 (18, p. 642). — Årronjarka, på svagt lappkulturpåverkad hedmark, 1922, G. Björkman (R). — Stora Sjöfallet, 1928, G. Björkman (16, p. 168); vid östra båtbryggan kring stugorna, 1935, A. Hülphers (R). — Sitojaure, 1870, E. J. Widmark (R, U). — Harsprångets telefonstation, 1931, E. Almquist (15, p. 168).

Gellivare: Luspebryggan, gräsvall vid byggnaderna, 1936, G. Björkman (R). — Suorva, ruderatmark, 1928—1929 (försvunnen 1936), G. Björkman (R, U; 16, p. 168). — Sitasjaures sydoststrand söder om Lietejokks utlopp, regio alpina, 1924, G. Björkman (R, U). — Från Lietejokks utlopp till Sitasjaures östända, spridd, 1924, G. Björkman (16, p. 41). — Vaisaluokta, på en öppen, grusig plats vid stranden, talrik. Lämningar av lappboningar i närheten, 1910, G. Jönsson [Ilien] (L). — Nedom Kaitumjåkko, 1894, N. Svensson [Wange] (R). — Vid Kaitumjokk flerstädes ända till norska gränsen, 1894, N. Svensson [Wange] (19, p. 4). — Killinge vid Kaitumälven, 1894, J. W. Hamner (R); Killinge, på backar vid Kaitumälven, 1897, N. Svensson [Wange] (L, R). — Gellivare, kyrkplatsen, 1868, V. F. Holm (R, U); 1928, R. Holmberg (L, U); — Silfwerbrands gård, 1904, H. Hesselman (R). — Vid vägen till Malmberget, 1921, G. Björkman (R). — Skaulo, 1928, O. R. Holmberg (L, U). — Moskojärvi, 1926, E. Nordström (R). — Kalixfors, vid turiststugan, 1917, M. Engstedt (R). — Paittasluspa, vid gården, 1920, C. G. Alm (31, p. 266).

TORNE LAPPMARK.

Jukkasjärvi: Vittangi kyrkby, 1864, L. Forelius (R, U); gårdsplan, 1942, S. Erlandsson (R). — Vittangi gästgivargård, 1928, B. Nilsson (R, U). — Kokkajärvi [mellan Vittangi och Sappisadsi], 1928, O. R. Holmberg (L). — Sappisadsi, hårdvall, 1907, A. Heintze (8, p. 53). — Övre Soppero, 1928, O. R. Holmberg (L). — Karhuvaara, 1918, H. E. Johansson (14, p. 486). — Junosuando Masugnsby, 1923, C. Th. Mörner (10, p. 134); 1941, A. Hülphers (R). — Svappavaara, gårdsplan i västra delen av byn, 1935, C. G. Alm (R, U). — Liukattijoki, landsvägskant, 1935, C. G. Alm (U). — Nykvarnijärvi, landsvägskant, 1935, C. G. Alm (U). — Altajärvi, odlad mark, 1935, C. G. Alm (R, U). — Jukkasjärvi kyrkby, 1852, R. F. Fristedt & F. J. Björnström

(R, U); äng vid prästgården och kyrkan, 1935, C. G. Alm (L, R, U). — Sevuvuoma, slåttermark, 1935, C. G. Alm (R, U). — Norra stranden av Oinakkajärvi, gångstig vid Homhujokis utlopp, 1926, C. G. Alm (R, U). — Kurravaara by, 1852, R. F. Fristedt & F. J. Björnström (R); 1905, M. Sondén (R). — Mellan Kallojärvi och Nuorajärvi, slåtteräng på udden norr om Kurravaara by, 1935 (L, R, U). — Tuolluvaara, vid landsvägen ca. 1 km öster om byn, 1935, C. G. Alm (L, R, U). — Tuolluvaara by, gräsmatta, 1939, C. G. Alm & H. Smith (R, U). — Vid gångstigen Kiruna-Kurravaara, väster om Nokutusvaara, 1929, C. G. Alm (R, U). — Luossavaaras sluttningar vid vägen Kiruna-Kurravaara, 1907, M. Sondén (20, p. 219). — Kiruna, vid [gamla] disponentbostaden, 1905, M. Sondén (R). — Kiruna, ca. 40 lokaler inom samhället, bolagets bostadsområde, »ön», Kirunavaara, järnvägens område väster om stationen samt nedersta delen av Luossavaaras södra sluttning, 1908—1909, H. G. Simmons (37, p. 55); betydligt sällsyntare åren 1920—1939, då förf. återfann växten endast på ett fåtal av dessa lokaler. — Vid vägen öster om Ala Lombolo, 1935, C. G. Alm (R, U); icke återfunnen här 1939. — På nya landsvägen Kiruna—Jänkänalusta, nära bron över Rakkurijokk, en tuva, 1939, C. G. Alm & H. Smith (U). — Vuoppevardo, 1920, C. G. Alm (31, p. 266). — Kaalasluspa, riklig, 1909, S. Birger (21, p. 211). — Båtplats vid Homhujokis utlopp i Kalixälven, trampad gräsmark, 1935, C. G. Alm (R, U). — Sakkivuoma, på gamla vägen Kiruna—Kalixälven, 1935, C. G. Alm (R, U). — Käyrävuopio, vid gården norr om sundet mellan sjön och selet i Rautasjoki, 1935, C. G. Alm (R, U). — Nakerijärvi, norra stranden, torr, sandig mark, 1880, K. P. Hägerström (L, R, U). — Vittjåtjåkko, 1920, H. Smith (U). — Vittjavares sydvästsluttning, brant med klipphyllor, »ej kulturpåverkad lokal», 1933, H. G. Bruun (R). — »In colliculo arenoso campi aperti inter alpes Barda et Kolkok et Tjuno et Soro prope Rautasjärvi», 1880, K. P. Hägerström (R, U); mellan fjället Kolkok [= Kålkotjåkko?] och Rautasjärvi, på sandkullar ymnig, 1880, K. P. Hägerström (22, p. 91). — Kuobletjåkko, 1920, H. Smith (U). — Kielaspuoltatjåkko, 1920, H. Smith (R, U). — Själlatjåkko mot Apporjaure, 1920, H. Smith (L, R, U). — Vid Vuolle och Paijeb Allesjaure, allmän, 1920, H. Smith (23, p. 445). — Paijeb Allesjaures sydöstra ända, vid kåtan, 1911, E. Almquist (24, p. 128). — Gardetjåkko, 1920, H. Smith (23, p. 445). — Ruopsuok, 1920, H. Smith (R, U); 1936, A. Nygren (U). — Sjangelitjåkko, sydvästpartiet, 1920, H. Smith (U). — Tjålmetjåkko mot Apporjaure, 1919, C. G. Alm (U). — Kartimavare, rengärde på nordsidan, 1919, C. G. Alm (25, p. 263). — I sänkan bakom Somaslaki, 1916, G. Erdtman (R, U). — Kierona, sydsidan, 1918, E. Asplund (R, U). — Fjället med höjdsiffran 812 SW om Abiskojaure, 1917, E. Asplund (U). — Påtsovare,

regio alpina, 1918, E. Asplund (U). — Kamavagge, vid renstig, 1934, A. Nygren (L, U). — Abiskojaures sydvästända, vid turiststugan, 1920, E. Nordström (R). — Vid Abiskojaure, 1909, L. Trafvenfelt (U); Abiskojaures väst- och sydstrand, 1916, G. Samuelsson (26, p. 38). — Abiskodalen, 1880, E. V. Ekstrand (27, p. 197). — Kårsonjuonje, gammalt rengärde, 1919, T. Å. Tengwall (26, p. 38). — Kårsovagge, flerstädes, regio alpina, 1915, E. Almquist (24, p. 126). — Tsasinnjaskatjåkko, regio alpina, 1916, G. Samuelsson (R); 700 m ö. h., 1927, G. Samuelsson & A. Zander (R). — Nuolja, 1906, K. Johansson (U); Nuoljas ost- och nordostsluttning ganska allmän till ca. 750 m ö. h., 1919, Th. C. E. Fries (26, p. 38). — Abisko, vid Marmorbrottet, 1919, T. Å. Tengwall (enligt uppgift). — På materialvägen mellan Abisko och Björkliden, 1923, Bertil Lindquist (U). — Vid bron över Kåppasjokk (strax öster om Björkliden), 1928, C. G. Alm (R, U). — Björkliden, materialvägen, 1936, R. Santesson (R). — Kedkevagge, 1913, N. Sylvén (29, p. 75). — Vassivagge, 1908, T. Lagerberg (R); 1913, N. Sylvén (29, p. 75). — Vassijaure Naturvetenskapliga station, ruderatmark, 1908, T. Lagerberg (28, p. [21]). — Räure, 1920. H. Smith (U). — Vaddetjåkko, SO-sluttningen, gräsmark i regio subalpina, 1903, N. Sylvén (30, p. 18). — Pålnoviken, båtplatsen nedom lapplägret, 1923, C. G. Alm (R, U). — Lulletjårro, regio alpina, 1918, E. Asplund (R, U); 1922, C. G. Alm (U). — Snuoratjåkko, vid Snuorajokk, 1919, Th. C. E. Fries (U). — Vid Jebrenjokk, 1926, O. R. Holmberg (L, U). — Pesisvare, regio alpina, 1916, G. Samuelsson (R, U); 1925, C. G. Alm (R, U). — Ortovare, 1913, N. Sylvén (U); 1927, R. Ohlsén (R). — Laimolahti, lapplägret, 1924, C. G. Alm (R, U). — Vid Pässinenjokks laguner (strax väster om Kaisepakte station), 1935, C. G. Alm (U). — **Karesuando:** Kyrkbyn, 1929, O. R. Holmberg (L); 1936, Eva Östrand (R). — Maunu, 1909, F. E. A. Block & A. T. Hwass (L, R, U); vid bastun, 1924, C. G. Alm & Fr. C. E. Fries (39, p. 253). — Kummavuopio [= Mukkavuoma], in prato, 1911, J. Montell (L, R, U); gårdsplan, 1924, C. G. Alm & Th. C. E. Fries (R). — Vaurakkakorva, 1909, Th. C. E. Fries & S. Mårtenson (32, p. [60]). — Gapovare, 1909, Th. C. E. Fries & S. Mårtenson (32, p. [60]). — Pältsa, 1919, C. G. Alm & T. Å. Tengwall (R).

Norge.

SÖR-TRÖNDELAG.

Glåmos: Stuedalsvollen, 1841, J. Ångström (R).

NORDLAND.

Nord-Rana: Dunderlandsdalen vid Storlie, 1870, H. W. Arnell (U). — Nevermoheia [= Nevernes?] i Dunderlandsdalen, 1870, A. Blytt (O). — **Ankenes:** Neverfjellets nordsida, 1929, A. Noto (O).

TROMS.

Bardu: På sørsiden av Altevatnet, 1886, O. Nyhuus (O). — Altevand, vid Strömmen, 1914, Th. C. E. Fries (U). — Under Kistefjell, 1886, O. Nyhuus (O). — Nedenfor Rokomborre, 1886, O. Nyhuus (O). — Hjerttind, 1879, J. M. Norman (O, R, U). — Skoelvdalen ved foten av Hjerttinden, 1879, J. M. Norman (R). — **Målselv:** Påvemoen ved Elvevollseteren, ved skogsgr. 300—400 m, 1886, O. Nyhuus (O). — **Balsfjord:** Tabmokdalen under Hattavarre (Nordgårdseteren), 1885, O. Nyhuus (O). — Svendborg, ved Fjellfroskvatnet, kring husene, 1885, O. Nyhuus (O); 1907, A. Landmark (R). — Markenesdalen, 1885, O. Nyhuus (L, O); Markenesdalen ca. 7 km fra sjøen, 1940, J. Devold (38, p. 13). — **Tromsöysund:** Tromsödalen, 300 m ö. h., 1899, A. Notø (R, U). — Tromsdalstind, 1841, M. N. Blytt (L, R, U); 350 m ö. h., 1899, A. Notø (U). — Flöjfjellet, 1924, C. Th. Mörner (R, U). — **Lyngen:** Rottenvikaksla ved Lyngseidet, 1919, R. Nordhagen (O).

Finland.

KEMI LAPPMARK.

Turtola: Äng vid Orajärvi gästgifveri, ymnig, 1919, J. Montell (33, p. 217). — **Kolari:** »in insula Yllässaari fluminis Muonio prope Simu in duobus pratis graminosis. Non antea in Fennia reperta.» 1877, Hj. Hjelt & R. Hult (34, p. 150). — Kolari kyrkby, in campo graminoso, 1922, M. J. Kotilainen (L, R, U); vid väg- och dikeskanter nära gästgifvaregården, 1943, A. Rantaniemi (enligt skriftligt meddelande från upptäckaren). — **Muonio:** Äng nära Muonio kyrkby, 1914, J. Montell (L, R, U). — »Käkinivavaara, invid ett gammalt skogsarbetarpörte vid stranden af en mosse (några få tufvor)», 1919, J. Montell (33, p. 217). — »På landsvägskant nära Eskelinen gästgifveri (en stor tufva)», 1919, J. Montell (33, p. 217). — Kihlanki, in prato, 1922, J. Montell (L, R, U). — Ylimuonio, in prato, 1942, J. Montell (L). — In pascuis ad pagum Tapojärvi, 1929, J. Montell (L, U).

Island.

Carex macloviana är enligt Johs. Gröntved, The Pteridophyta and spermatophyta of Iceland (The Botany of Iceland, vol. IV, part I, 1942, p. 160) känd från ca. 40 lokaler på Island. De allra flesta av dessa ligga omkring Eyjafjörður och Myvatn i öns nordligaste del, medan några få lokaler ligga spridda i mellersta delen. Den sydligaste fyndorten, Arnarfjell hið mikla, ligger strax söder om Hofs-jökull. Första fyndet gjordes av C. Grønlund år 1876 vid Helluvað nära Myvatn. För övrigt hänvisar jag till det citerade arbetet av Gröntved, som på en karta utmärkt samtliga kända lokaler för *Carex macloviana* på Island.

4. Invandrings- och spridningshistoria i Fennoskandia.

Carex macloviana hör till den grupp nordiska fjällväxter, som sedan gammalt kallats västarktiska, varmed menas sådana arter, vilkas cirkumpolära utbredning sträcker sig från Grönland genom arktiska Nordamerika till Sibirien men ej längre västerut än till floden Lenas mynning, och som kommit till Fennoskandia från väster. På vad sätt och under vilken geologisk period invandringen skett är ett problem, som intresserat många växtgeografer och olika åsikter ha framförts. Enligt en teori, som bl. a. den norske botanisten A. Nɔtø anslutit sig till, är *C. macloviana* en interglacial invandrare. Han skriver om denna (36, p. 174): »Dens nærmeste slægting er *C. Leporina* L., som er meget utbret i det boreale planterike. Av denne er *C. festiva* ubetinget opstaat. Dens ankomst hit maa være sket i interglacialtiden; men da den ikke findes mellem Kamtschatka og Muonio, kan der neppe være tal om landeveien. Den er fra det nordlige Nordamerika, hvor den er utdifferentiert henimot istiden, transportert hit med drivisen.» Säkert oriktig är den framställning om denna arts invandring, som publicerats av H. G. Simmons år 1910 i »Floran och vegetationen i Kiruna», p. 54: »Artens utbredning i norra Skandinavien (de norra svenska lappmarkerna, i Norge ned till Ranen och i finska lappmarken) i förening med att den hufvudsakligen håller sig i högre trakter (i Ranen går den dock ända ned till 30 m. ö. h.) tyckes mig otvetydigt anvisa den en plats i den grupp af hufvudsakligen alpina arter, som invandrat från Nordryssland och inom Skandinavien spridt sig söderut. En jämförelse mellan dess utbredning och t. ex. förekomsten av *Pedicularis hirsuta* och *P. flammea* visar en så nära öfverensstämmelse, att den knappast kan vara tillfällig. Äfven dess utbredning utom Skandinavien synes mig peka i samma riktning, och den lucka i dess område, som med vår nuvarande kännedom om Sibiriens och Nordrysslands flora förefinnes, torde kanske ännu fyllas genom kommande undersökningar.» Mer än 30 år ha förflutit sedan Simmons skrev detta och antalet fyndorter för *C. macloviana* i Fennoskandia, framförallt i Sverige, har mångdubblats. Samtliga finska lokaler ligga mindre än 10 km från Torneälv och Muonioälv, där dessa bilda

gräns mot Sverige. Trots att många botanister gjort forskningsresor i Nordryssland och Sibirien, saknas fortfarande fynd av *C. macloviana* väster om Kamtschatka. Det är mig oförklarligt, varför Simmons jämför utbredningen i och utom Skandinavien mellan denna och de bägge *Pedicularis*-arterna och finner en »nära öfverensstämmelse».

Om man med ledning av den nuvarande utbredningen sådan den återges på kartbilden skulle våga draga någon slutsats om var *Carex macloviana* överlevat den sista skandinaviska istiden, kan denna knappast bli annat, än att denna art måste haft refugier mellan Lofoten och Salten fjord. Dock torde de nutida norska lokalerna i närheten av kusten med hänsyn till spridningsmöjligheterna knappast kunna betraktas såsom de primära. Vore så fallet, borde växten förekomma på många ställen efter norska kusten i Troms och Nordland liksom på dalbottnarna långt in i landet. I detta sammanhang bör framhållas, att det är ovisst om *C. macloviana* fortfarande finnes kvar på alla de norska lokaler, som äro upptagna på kartan och uppräknas i texten. Förekomsten vid Stuedalsvollen, endast bekant genom J. Ångströms fynd år 1841, torde med all säkerhet varit tillfällig. Floran i Sör-Tröndelag är så väl känd, att denna växt icke gärna kunnat undgå att observeras under de 100 år, som sedan dess förflutit. Flertalet av dessa fynd gjordes på 1870- och 1880-talen och oftast saknas herbariematerial och litteraturuppgifter av senare datum. Ytterst få nya lokaler ha upptäckts i Norge under de sista 50 åren. Helt annorlunda ligger saken till i Sverige. Medan man år 1890 endast kände ett 20-tal fyndplatser, uppgå dessa nu till ca. 180. Av dessa svenska lokaler ligger ungefär hälften inom fjällområdet och hälften i barrskogslandet. På grund av svårigheten med forskningsresor i fjällen i forna dagar, bör man ej förvåna sig över att före K. P. Hägerströms och E. V. Ekstrands färd genom Torne Lappmark år 1880 var ingen lokal bekant från det svenska högfjällsområdet. Av kartan framgår att det stora flertalet lokaler från fjällområdet ligga i Lule Lappmark samt i Torne Lappmark norrut till Torneträsk. Tyvärr är utbredningen i höjdled föga undersökt. I allmänhet torde de högsta lokalerna ligga vid eller obetydligt ovanför björkskogsgränsen, d. v. s. inom området för artens

utbredning högst 800 m ö. h. Uppgifter om högre belägna fyndorter saknas alldeles.

Redan tidigt lade man märke till, att *Carex macloviana* så gott som alltid förekom vid stigar, på vägkanter, gårdsplaner, slåtterängar och odlad mark inom skogsområdet. Härav drog man den slutsatsen, att den var kulturgynnad och med största sannolikhet spreds genom människor och husdjur. I samband med publicerandet av det för Finland nya fyndet av *Carex macloviana* på två ängar på ön Yllässaari i Kolari (34, p. 98) skriver R. Hult: »Dessa ängar hade uppstått af gamla odlingar; tegar och diken funnos ännu qvar. Hvarifrån hade *C. festiva* i så sen tid kommit dit? Antingen med utsädeshöfrö från svenska lappmarken eller med foglar på flyttning eller sannolikast finnes den på någon äldre ståndort i närheten. Kan således vidare eftersökas med hopp om framgång.» A. Heintze, som mera ingående studerat spridningen av *Carex macloviana* under en resa för 40 år sedan i övre Norrbotten och angränsande delar av Torne Lappmark samt i Nordnorge, framlägger utförligt sin åsikt härom (8, p. 52—53) och jag citerar följande: »En annan växt, som synbarligen [liksom *Rubus arcticus*, *Polemonium* **campanulatum* och *Veronica longifolia*] har lappar och finnar att tacka för sin spridning till — eller åtminstone inom — Skandinavien, är *Carex festiva*.» — »Från Pajala och Kengis följer *Carex festiva* landsvägen till Wittangi och Svappavaara. Efter den nya vägen från Wittangi till Soppero har växten ej trängt fram längre än till första skjutsstationen, Sappisadsi (Hvilan), där den ännu är mycket sparsam. Nordväst om Svappavaara är *Carex festiva* känd från Kiruna, Jukkasjärvi och Kurravaara; vidare vid Nakerijärvi och därifrån på sandkullar upp mot Rautasjärvilapparnas sommarvisten. Strax inom norska gränsen och norrut från Kattovuoma växer *Carex festiva* invid Altevand och därifrån längs älfvarna och lappflyttningsvägarna ut till hafvet, på ett par ställen något utom fjordbottnen. [Tromsdalstind och Flöjfjellet?]» — Vid Sappisadsi förekom den i en »gammal» starkt gödslad timotejvall tillsammans med en del kultur- och ruderatväxter, t. ex. *Phleum pratense*, *Trifolium pratense*, *Veronica longifolia* och *Rumex domesticus*. Heintze anser *C. festiva* införd med hästgödsel, varpå han tyder dess spridning utmed lands-

vägarna. »Ofvan barrskogsgränsen synes spridningen till väsentlig del ha verkställts af renen, och med tillhjälp af detta djur har växten troligen nått fram till sina norska växtplatser.» Helt motsatt åsikt framlägges av Simmons i det förut citerade arbetet (37, p. 54): »Att den, såsom A. Heintze tror, 'synbarligen har lappar och finnar att tacka för sin spridning till — eller åtminstone inom — Skandinavien', måste betecknas såsom ett skäligen löst antagande. Om så vore, borde det ju förvåna, att den icke vunnit insteg i något enda af de sydligare af lappar och finnar bebodda områdena. Heintzes antagande motsäges också af dess sällsynthet i de finska lappmarkerna, där Hjelts Conspectus blott upptar en enda lokal. Mig synes intet vägande skäl föreligga, att betrakta dess utbredning såsom beroende på införsel med menniskans hjelp. En annan sak är, att den tydligen är en kulturälskande art, som vunnit nya växtplatser genom menniskors åtgörande. Dess förkärlek för öppna, gräsbevuxna lokaler gör nämligen, att den i opåverkad mark ej finner många ställen, där den kan trifvas, men att kulturen efter hand bereder den möjlighet att skaffa sig en mängd nya växtplatser i trakter, där den förut varit sällsynt. Inom Kiruna-området är den tydligen i stark spridning.» Björkman (16, p. 40) anser *Carex macloviana* »knappast någonstädes vara inhemsk. Sannolikt införd genom lappkulturen, vare sig det nu skett genom lapparna själva eller deras renar, eller kanske genom bådadera.» Ett antal lokaler, som tydligen tillkommit i sen tid, behandlar han i samband med en förteckning över ruderatfloran inom det undersökta området (utmed sjöarna och Stora Luleälv från Suorva-dammens uppdämningsområde till Porjus).

Under mina färder i Lappland så gott som varje sommar från 1919 till 1939 har jag begagnat varje tillfälle undersöka växtlokaler för *Carex macloviana*. Tyvärr måste jag medge, att jag aldrig påträffat denna på någon lokal, som icke på ett eller annat sätt visat spår efter människor, renar eller varit vad man kallar »kulturpåverkad». Jag har sett denna växt i massförekomst i en insåning vid gården Märsa i Arjeplog och på en äng vid Jukkasjärvi kyrka och prästgård, på gårdsplaner och vägkanter mångenstädes i de tre nordliga lappmarkerna samt vid lappläger, kåtaplatser, rengärden och renstigar. Ovan

björkskogsgränsen på fjällen omkring Torneträsk och i nordligaste Karesuando har jag aldrig funnit ett enda exemplar annorstädes än vid renstigar och kåtaplatser använda vid lapparnas flyttningar. Två gånger har jag sett anteckningar på växtetiketter om att insamlingen skett på en »naturlig» ståndort. Emellertid tror jag knappast det finnes någon växtplats för *C. macloviana* så belägen, att den icke någon gång trampats av lappar eller renar. Ty i likhet med Björkman är jag av den meningen, att spridning i fjällen knappast kan ske på annat sätt, trots att varken jag eller någon annan iakttagit *C. macloviana*-utrikler eller -ax med sådana fästade på renar eller på pälsar eller fällar av renskinn. Även flertalet lokaler i barrskogsområdet hava helt säkert spridning med lappar och renar att tacka för sin tillkomst. Samtliga svenska lokaler ligga inom det område, som beröres av lapparnas höstflyttningar från fjällen. Endast ett par lokaler längst ned i Tornedalen ligga strax utanför gränsen för flyttningarna. Dessa förekomster kunna liksom många andra inom området bero på lokal spridning, men i detta speciella fall finnes möjlighet för transport med de renar, som användes såsom dragdjur, då järnmalm fraktades från Luossavaara och andra järngruvor till Kengis m. fl. bruk i Tornedalen. En blick på kartan visar huru skogslandets lokaler ligga i rad efter älvdalarna, där flyttningsvägarna gå fram. På vad sätt spridningen fortsättes från lokal till lokal efter en väg eller från en gård till en annan är icke utrett. Det synes mig emellertid icke sannolikt, att detta såsom Heintze menar skulle ske med hästspillning. Carex-utriklerna lämna föga skydd för fröna under passagen genom växtätande djurs matsmältningskanal. Troligaste spridningssättet i låglandet förefaller mig att vara med hö eller s. k. höfrö, vilket väl än idag sopas upp från ladbottnarna och användes för insåning av fleråriga vallar. Men epizoisk spridning med husdjur är även möjlig.

Om man antager, att renar och lappar i huvudsak sörja för spridningen från fjällen mot väster, får man en plausibel förklaring till att *C. macloviana* är så sällsynt i Norge. Under förutsättning att denna arts primärlokaler numera i huvudsak äro belägna inom den svenska delen av fjällkedjan, kunde även under den långa tid, då svenska lappar varje vår flyttade ned

till norska kusten, några spridningsenheter av *Carex macloviana* icke följa med i större skala, emedan denna flyttning skedde på senvintern, då marken och alla örter ännu voro täckta av djup snö. Endast i Tromsdalen, dit ett stort antal svenska renar årligen flyttade, kan det vara sannolikt, att en tillfällig spridning skett med dessa, liksom till lokalen på Lyngseidet. För övrigt må framhållas, att utom tamrenar funnos i nordligaste Sverige vildrenar ännu på 1830-talet och spridning med sådana har naturligtvis varit lika möjlig.

Förekomsterna i Finland, som ju nära ansluta sig till dem på svenska sidan om gränsälvarna, torde med all sannolikhet uppkommit genom transport med höfrö från Sverige, såsom också Hult framhållit redan vid publiceringen av fyndet på Yllässaari i Kolari. Vilken av de finska lokalerna som är den första, där växten först naturaliserats och varifrån sedan sekundärspridning skett, torde vara omöjligt fastställa.

Av det nu anförda i fråga om artens spridning torde med all tydlighet framgå, att Simmons påstående, att denna sker oberoende av människor och djur, är, för att använda hans eget uttryck om Heintzes teori, »ett skäligen löst antagande». Om spridningen utan speciell medverkan från dessa kunde ske till »öppna, gräsbevuxna lokaler», skulle säkerligen *Carex macloviana* vara en av norra Fennoskandias vanligaste arter, både på skogsområdets odlade mark och på fjällområdets vidsträckta ängar och gräshedar.

Mot Simmon's argument, att *C. macloviana*, om dess spridning skedde med hjälp av lappar och renar, borde finnas även i Jämtland, Härjedalen och norra Dalarne, behöver blott hänvisas till det faktum, att renarnas vandring eller lapparnas höstflyttning aldrig sker från norr mot söder på grund av geografiska hinder och alltså en spridning söderut på detta sätt icke är tänkbar.

Summary.

Most probably *Carex macloviana* was first collected by the famous phyto-geographer G. Wallenberg during some of his four botanical journeys in Lapland in the beginning of the 19th century. He gave some specimens to the young Candi-

date of Medicine C. Hartman, who described this plant in 1820 in the first edition of "Handbok i Skandinaviens flora", but only as a variety β *ovata* of *Carex leporina* L. Some years later it was found by Dr. J. Richardson in Arctic America at Bear Lake and on the Rocky Mountains and was described by Professor C. Dewey, who named it *Carex festiva* in 1836. Professor Elias Fries, who in 1841 received specimens of this plant, hitherto named in Europe *C. leporina* β *ovata,* from Professor M. N. Blytt, who had collected it the same year near Tromsö in Arctic Norway, proved that it was identical with *Carex festiva* Dewey. Fries distributed Blytt's plant in Herbarium Normale, Fasc. VIII, No. 82 in 1842. The statement of K. K. Mackenzie in North American Flora, Vol. 18, that *C. leporina* L. β *ovata* "Laest." is typical *C. leporina* L. is erroneous. As early as 1826 the French naval officer and naturalist Dumon D'Urville had described his *Carex macloviana*, collected by himself in the Falkland Islands during Duperrey's Antarctic expedition in the ship Coquelle. In his monograph on *Caricoideae* in Engler's Pflanzenreich, IV: 20, (1909), the Rev. G. Kükenthal proved that *Carex festiva* and *C. macloviana* were identical and that the latter was the correct name.

Carex macloviana s. str. is known from Arctic Northwestern Europe (Sweden, Norway, Finland and Iceland), Greenland, Arctic North America from the Gaspé Peninsula and Labrador to Mackenzie River, South America from Ecuador to Patagonia and Tierra del Fuego, the Falkland Islands, Hawaii, the Northern Kuriles and Kamtchatka. The distribution in Fennoscandia is marked on the map with a dot for each locality. In all about 200 localities are reported, most of them in Northern Sweden. More then 9/10 of the 180 finds in Sweden were made after 1900.

C. macloviana most probably survived the last glaciation in Northern Europe on refuges free from ice. Nowadays this plant is known from only very few stations close to the Norwegian coast and to these it has reimmigrated fairly recently from its localities in the high mountains. About half of the Swedish localities are situated in the northern mountain region of Lapland, the other half in the northern region

of the coniferous woods. In the mountains very few finds are reported other than near the huts of Lapps, at paths trodden by reindeer etc. It is the present author's opinion that *C. macloviana* is dispersed mainly by Lapps and their reindeer, a theory initiated by Swedish phyto-geographers many years ago. Every autumn the reindeer move from the mountains eastwards and spend the winter in the pine-woods, often not far from the Gulf of Bothnia. *C. macloviana* is hardly found outside the region visited by Lapps and reindeer. In the forest region most of the stations of this plant are cultivated ground, domestic lawns, road-sides etc.

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Orchis strictifolia Opiz var. *ochroleuca* (Boll) Hyl., en förbisedd svensk kalkkärrväxt.

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Dactylorchis, d. v. s. den sektion inom släktet *Orchis*, som utmärkes av flikade (eller åtminstone nedåt tillspetsade) knölar och örtartade högblad, kan i den nordiska floran indelas i tre artgrupper, nämligen *O. sambucina*-gruppen, *O. maculata*-gruppen och *O. latifolia*-gruppen.

Den första gruppen representeras i hela Mellan- och Nordeuropa av en enda mycket enhetlig art, *O. sambucina* L., »Adam och Eva», som väcker allmän uppmärksamhet genom de två färgformer, varunder den regelbundet uppträder, en med blekgula blommor och en med mättat röda till purpurröda blommor med vid basen gulfläckig läpp. Utom dessa bägge former förekomma dock stundom exemplar med blekare, rosen- eller köttröda blommor; och det är på sådana bleka exemplar, som namnet *O. incarnata* L. ursprungligen synes syfta, såsom bl. a. C. J. Hartman (1) och Pugsley (2) sökt leda i bevis, ehuru namnet i regel använts om en art av den tredje artgruppen, *O. strictifolia* Opiz.

Även den andra artgruppen representeras i svensk floristisk litteratur av en enda art, *O. maculata* L., men denna vårt lands utan jämförelse allmännaste *Orchis*-art är, som allmänt bekant, synnerligen mångformig. Genom undersökningar av Hagerup (3) på danskt material ävensom av Vermeulen (4) och Heusser (5) på nederländskt(?) resp. schweiziskt har den visats innehålla såväl diploida ($n = 20$) som tetraploida ($n = 40$) typer. De förra, som såväl i Danmark som i Schweiz äro de avgjort sällsyntare, representeras i Danmark av en bokskogsform från Møens kritformation, som av Hagerup identifierats med var. *Meyeri*

Rchb. fil.[1] och sedermera av Wiinstedt (6) upptagits som skild art. Synonym härtill är uppenbarligen den av Neuman (7 p. 152) från Sydsverige beskrivna var. *obscura* Neum., vilken synes ha en vidsträckt utbredning i vårt lands kalkrikare trakter. Även i Storbritannien har denna typ uppmärksammats och beskrivits som art under namn av *O. Fuchsii* Druce (8), varefter en rik litteratur (9) om de olika *O. maculata*-typerna sett dagen. Namnet *O. Fuchsii* har i förbigående anförts av Lindman i andra upplagan av hans flora (10). Denna, som det vill synas, ganska enhetliga typs begränsning gentemot de mycket mångskiftande tetraploiderna är ännu alldeles oklar och fordrar ingående studier.

Den tredje artgruppen, *O. latifolia*-gruppen, åter har sedan gammalt med full rätt ansetts som en av vår floras mera kritiska grupper. Efter E. Fries (11) har dock blott en svensk botanist mera utförligt i tryck framlagt studier däröver, nämligen Neuman (5), vilken jämte en rad former av lägre rang nybeskrivit ej mindre än tre nya arter (*O. longifolia*, *O. pseudocordigera* och *O. cruentiformis*) utan att dock väsentligt ha bidragit till gruppens utredande. En ingående, på lång sikt lagd undersökning över spec. de gotländska typerna är emellertid sedan några år påbörjad av fil. lic. Bengt Pettersson.

Utanför Skandinavien har gruppen de senaste decennierna varit föremål för ivrigt arbete. Detta gäller framförallt Storbritannien, varifrån en rad viktiga arbeten över »Marsh Orchids» med åtskilliga nya arter publicerats av bl. a. Druce, Godfery, T. & T. A. Stephenson, Wilmott och Pugsley (2, 12, där även hänvisningar till övrig brittisk litteratur finnas). En av de nya arterna, *O. purpurella* T. & T. A. Stephens., har f. ö. sedermera påvisats som förekommande i västligaste Danmark (Vendsyssel) (6) och i västra Norge (13). — Hela artgruppen är vidare föremål för en ingående revision av holländaren, dr. P. Vermeulen, som publicerat några mindre arbeten häröver (4, 14).

Av de svenska arterna är *O. strictifolia* Opiz (= *O. incarnata* auctt.) den allmännaste och väl också den mångformigaste. Närmaste anledningen till detta meddelande är en av dess

[1] Även Vermeulen betecknar sin diploid med samma namn.

former, var. *ochroleuca* (Boll) Hyl., vilken jag redan under gymnasiståren stiftade bekantskap med på Kärna mosse vid Linköping och som redan då frapperade mig genom sitt från vanlig *O. strictifolia* avvikande utseende och genom att ej uppträda i sällskap med denna. Under en försommaren 1943 företagen studentexkursion till Omberg fick jag i de rika kalkkärren vid bergets östra fot återse denna egendomliga typ, som ej heller där förekom tillsammans med vanlig *O. strictifolia* men däremot med *O. cruenta* O. F. Müll. En granskning av litteraturen samt av materialet i Naturhistoriska Riksmuseums Botaniska Avdelning i Stockholm (S), Uppsala Botaniska Museum (U) och Göteborgs Botaniska Trädgård (G)[1] jämte välvilliga upplysningar och översända exemplar från ett antal botanister, bland vilka må nämnas fil. lic. N. Albertson, regementsläkare E. Th. Fries, civilingeniör J. Hallberg, telegrafkommissarie Th. Lange, telegrafkommissarie H. Nilsson, fil. kand. G. Sandberg, lektor R. Sterner, professor The Svedberg, docent H. Weimarck och fil. kand. G. A. Westfeldt har givit vid handen, att det här med största sannolikhet rör sig om en distinkt typ med särskild utbredning och särskild ekologi och således ej blott om en färgform (albino) av *O. strictifolia*.[2]

Tidigast uppmärksammades vår typ i Östergötland, där Wessén (16) redan 1838 från »Jacobslunds mosse» i Kärna meddelade en *O. latifolia* var. *floribus albis*. Under det följande decenniet studerades de östgötska formerna av artgruppen intensivt av bröderna Holmgren (Hjalmar, sedermera prof. i matematik och matematisk fysik vid Tekniska högskolan, Karl Al-

[1] Lunds Botaniska Museums hela material av artgruppen är utlånat till dr. Vermeulen och har på grund av tidsförhållandena ej kunnat återfås, varför jag ej kunnat beakta detsamma. Delar av Stockholms- och Uppsalaherbarierna äro likaledes hos honom.

[2] En verklig albino synes också förekomma, ehuru mycket sällsynt. Själv har jag icke haft tillfälle se en sådan vare sig levande eller pressad, ej heller har jag mottagit någon säker uppgift om sådan i Sverige. Uppgiften om *O. incarnata* f. *ochroleuca* från en lokal i norra Dalarna (15) hänför sig möjligen till en sådan. Denna albino har, liksom motsvarande form av exempelvis *O. maculata*, rent vita (ej gulvita) blommor och uppträder enstaka bland exemplar med normal blomfärg. Former med rent vita blommor med svagt rosafärgade teckningar på läppen beskrivas även i den utländska litteraturen.

BERT sedermera prof. i fysik i Lund, och FRITHIOF, sedermera prof. i fysiologi i Uppsala), vilka alla iakttogo denna typ på östgöta-siluren. CARL FRIES (17) publicerade 1922 ett fotografi av den härifrån; och HESSELMAN (18) har ägnat ett ingående intresse åt denna typ, som han träffande karakteriserar som »en av Ombergs vackraste orchideer, där den står i kärren som grupper av raka vaxljus».

Nära nog samtidigt med i Östergötland anträffades typen på Gotland, nämligen 1840 av C. F. NYMAN och 1841 av P. C. AFZELIUS. Den senares insamling (från Snäckgärdet vid Visby) utdelades följande år i Herb. norm. (VII: 66) under namn av *O. incarnata* var. *alba* Afz. fil.[1]. Sedermera har den flitigt samlats på Gotland och är nu känd från bortemot 30 lokaler. Även härifrån ha fotografier publicerats (23, fig. 2 och 25), vilka enligt meddelande av fil. kand. G. SANDBERG representera vår typ.

Även på Öland iakttogs vår typ ganska tidigt eller redan 1853, då FLODERUS insamlade den vid Mörbylånga (väster om Borgby borg) och följande år publicerade den som *O. incarnata* var. *albiflora* (24). STERNER (25) uppger den vara »nicht selten», men antalet kända lokaler är alltjämt ganska obetydligt. Lektor STERNER har välvilligt ställt sina anteckningar till mitt förfogande och meddelat, att lokalerna säkerligen äro vida talrikare, då han ej konsekvent hållit denna typ isär från övrig *O. strictifolia*.

Från ett fjärde svenskt landskap blev den ej känd förrän 1902, då WITTE (26) meddelade en lokal från Västergötland (Åsle: Svarttorp) av *O. incarnata c. fl. alb.* Senare ha ytter-

[1] Detta namn, åtföljt av anmärkningen »Labelli lobo medio producto insignis. *Latifolia* simul.» måste betraktas som ett *nomen (sub-)nudum*. Då det ej upptagits i senare svensk floristisk litteratur, ej ens i E. FRIES' bearbetningar (11) av artgruppen eller i någon upplaga av HARTMAN's Flora, är det lättförklarligt, att typen blivit försummad hos oss. — Närmast yngre namn (1851) »*O. incarnata* a. *lanceata straminea*» Rchb. fil. (19 p. 183) är likaledes ett *nomen nudum*. — Namnet *O. incarnata* β *ochroleuca* Boll (20) är däremot giltigt publicerat. Citatet hos PUGSLEY (12 b p. 52) »β *ochroleuca* (Wustnei)» är falskt, då parentesen »(Wüstn. 1854)» enligt BOLL's teckenförklaring betyder, att växten för första gången angavs såsom förekommande i Mecklenburg av WÜSTNEI (21) 1854, men ej har någon hänsyftning på namnet. Den nu giltiga kombinationen under *O. strictifolia* gjordes 1942 av HYLANDER (22).

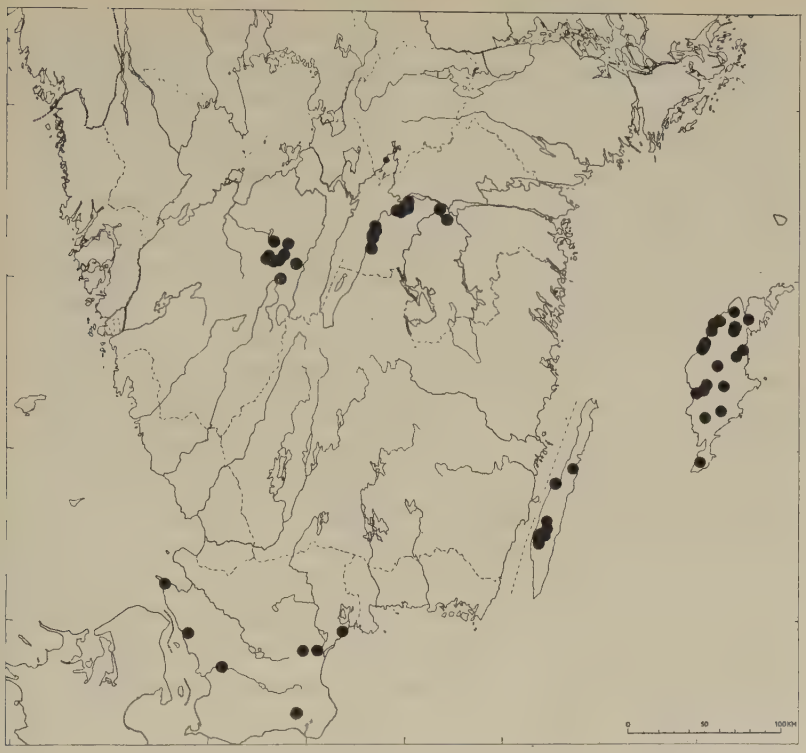

Fig. 1. Den svenska utbredningen av *O. strictifolia* var. *ochroleuca*. (The Swedish distribution of *O. strictifolia* var. *ochroleuca*).

ligare ett 10-tal lokaler blivit kända, samtliga inom silurområdet. Anmärkas må, att typen ej anträffats på Kinnekulle (där även *Schoenus ferrugineus* saknas) eller på Billingen.

Genom min herbariegranskning och korrespondens med samlare ha några lokaler från ännu ett landskap. Skåne, bragts i dagen.

Typens svenska utbredning, sådan den framgår av ovanstående karta (fig. 1) och av bifogade lokalförteckning, ger den en plats bland våra mest kalkkrävande växter. Ekologiskt är den också inskränkt till extremrikkärren (enligt Du Rietz' terminologi, 27, jfr även 28). Den synes särskilt förekomma i *Schoenus ferrugineus*-kärr. För samtliga östgötska och västgötska fyndställen, där växtsamhället är närmare känt, uppges sålunda dylika ståndorter. Detsamma gäller alla av dr. E. Th. Fries meddelade gotländska fynd, med undantag av

ett (Othem: Pussmyr), där den förekom i *Cladium*-myr. För Ölands vidkommande meddelar mig lektor Sterner, att ståndorterna äro mera växlande och utgöras ej blott av de på Öland mindre allmänna *Schoenus*-kärren utan även av andra kalksamhällen, såsom *Carex Hostiana*-kärr och *Sesleria*-ängar. I Skåne synes den likaledes förekomma ej blott i *Schoenus*-kärr utan även i andra extremrikkärr.

Vår typ avviker sålunda starkt till såväl utbredning som ekologi från rödblommig *O. strictifolia*, vilken ju förekommer över större delen av landet och visserligen synes vara tydligt kalkgynnad men ingalunda är så strängt kalkbunden samt växer i ganska skiftande växtsamhällen, fuktängar, kärrängar och kärr.

Den här meddelade fyndortsförteckningen gör naturligtvis ej anspråk på att vara fullständig. Antalet fyndorter på Gotland och Öland samt framför allt i Skåne, i vilket senare landskap den hittills uppenbarligen ej blivit systematiskt eftersökt, torde vid fortsatta studier bli kraftigt utökat. Däremot är det knappast att vänta, att den skall anträffas inom något nytt område, då de trakter (Stockholms skärgårds kalköar, det kalkrika Älvkarleby-Gävle-området och Jämtlandssiluren), vars jordmån synes bäst lämpad, äro botaniskt väl undersökta, icke minst med avseende på orchidé-floran[1]. Beträffande Jämtland har telegrafkommissarie Lange meddelat mig, att han aldrig därstädes anträffat någon gulvit eller vit *O. strictifolia*.

Från Danmark är typen mig känd från två lokaler, men här kan antalet sannolikt bli starkt utökat. I Norge är typens förekomst sannolik (13), ehuru jag ej sett något exemplar och ej känner någon preciserad lokal.

Utomskandinaviska exemplar har jag blott sett från några få lokaler i Tyskland och Österrike, men dessa överensstämma noga med det svenska materialet. Enligt dessa och trovärdiga litteraturuppgifter (ev. med illustrationer) ter sig totalutbredningen på följande sätt.

I England är typen sällsynt och känd med säkerhet endast från Norfolk. Huruvida den förekommer i Frankrike, är tvivel-

[1] Litteraturuppgiften (15) från norra Dalarna hänför sig, som ovan antytts, sannolikt till en verklig albino-form. Något belägg-exemplar har ej varit mig tillgängligt.

aktigt; i varje fall tycks den vara en stor sällsynthet där. I Nordtyskland har den en rätt stor utbredning; den är sällsynt i Rheinland (en enda lokal), men allmännare österut (Mecklenburg, Brandenburg, Pommern, Posen), vilken nordosttyska utbredning enligt ZIEGENSPECK (29 p. 626) ungefär sammanfaller »mit der Zone der wenig ausgelaugten Teile der Moräne». Likaså torde den ej vara alltför sällsynt i de baltiska länderna, där uppgifter föreligga åtminstone från Lettland och Estland I mellersta Tyskland synes den saknas, men uppträder ånyo i Alpländerna: sydligaste Baden, Württemberg, Bayern[1], norra Schweiz (kantonerna Waadt, Aargau, Zürich, Schwyz, Graubünden), Liechtenstein, Vorarlberg, Tirol, Nieder-Österreich, varjämte uppgifter föreligga från Polen, Ungern och Rumänien.

Om typens ekologi i Mellaneuropa är föga känt. ZIEGENSPECK (29) anför dock »sehr kalkreiche Schoeneten» (p. 591) och »Kalksintermoore» (p. 733) som karakteristiska ståndorter för den med *O. palustris* som följeväxt; han uppger (p. 625) den vidare i Sydtyskland växa »auf stark kalkreichen Wiesenmooren». Det förefaller emellertid, som om den i Mellaneuropa ej vore lika exklusiv som i Sverige, något som ej vore att förvåna sig över, då ju växter ofta vid gränsen för sin utbredning bli mera nogräknade med avseende på sina ståndorter.

De systematiska karaktärer, som utmärka denna typ äro föga markerade med undantag för blomfärgen. Denna kan närmast betecknas som benvit med klarare gul underläpp och denna saknar varje teckning. Tillsammans med de ljust gröna till grönvita högbladen får blomställningen sålunda sedd på avstånd en tydligt vaxgul färg. Läppen är alltid tydligt treflikad med ofta utdragen mittflik och snett framåtriktade sidoflikar (fig. 2), en läppform, som visserligen kan förekomma även hos andra *O. strictifolia*-typer men som ingalunda är

[1] I Bayern synes utom vår typ förekomma en annan, rent vit, nämligen den av REICHENBACH FIL. (19 p. 183) som *albida parviflora*» omnämnda, varmed sannolikt är identisk VOLLMANN's (30) var. *albiflorus* Lec. & Lam., som karakteriseras »Blt. weiss. Meist in grösseren Beständen, nicht nur vereinzelter Albinismus» i motsats till var. *ochroleucus* »Blt. hellgelb. So streckenweise in grösseren Beständen. Bltzeit um 2—3 Wochen später.» Någon sådan vitblommig typ tycks ej finnas i Norden.

vanlig inom arten. Läppstorleken hos vår typ håller sig omkring 5—7 × 5—8 mm. och sporrens längd omkring 7—8 mm. En vacker färgbild finnes hos Nelson (31 taf. 5 fig. 12), en teckning hos Hegi (33 a fig. 431, 33 b fig. 678) och fotografier av blommor och blomställningar hos Keller & Schlechter (32 tab. 207 fig. 2, tab. 361 fig. 1—3, tab. 362 fig. 2). — Typen är hos oss i regel rel. lågvuxen men styv och kraftig. Bladen äro från bred bas tämligen rätlinjigt smalnande mot spetsen och styvt uppräta. Blomningstiden är enligt Hesselman (18), Vollmann (30) och Fischer (31) senare än hos de vanliga röda typerna.

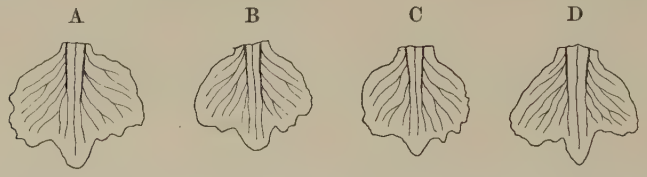

Fig. 2. Underläppar av *O. strictifolia* var. *ochroleuca*. (Lips of *O. strictifolia* var. *ochroleuca*.) A. Östergötland: Hagebyhöga, 10. VII. 1853, J. E. Zetterstedt. — B. Västergötland: Åsle, 4. VII. 1932, J. A. O. Skårman. — C. Östergötland: Väversunda, 4. VI. 1943, J. A. Nannfeldt (n. 6449). — D. Gotland: Stenkyrka, 2. VII. 1914, K. Johansson. 2 ×. H. Smith del.

Såvitt det kan bedömas är sålunda denna typ, vilken lämpligen bör givas varietetsrang, mycket enhetlig och i allmänhet skarpt avgränsad[1]. Uppenbarligen hybridiserar den dock med närstående typer. Enligt Heusser överensstämmer den med övrig *O. strictifolia* och med *O. cruenta* i att vara diploid ($2n = 40$), under det att *O. majalis* och *O. purpurella* äro tetraploider ($2n = 80$) och *O. Traunsteineri* synes innehålla både diploida ($2n = 40$), tetraploida ($2n = 80$) och hexaploida ($2n$ = c. 122) typer (4, 5). — På en av K. A. Holmgren författad etikett (i S) med utförlig latinsk diagnos av vår typ anmärker han, att denna förekommer »äfven, ehuru mera sällan, med purpurascenta blommor och har då understundom fläckiga blad». Tyvärr finnas inga sådana exemplar bevarade, ty de kunna knappast ha varit annat än hybrider med *O. cruenta*, tillsam-

[1] För dess systematiska självständighet ha också talrika mellaneuropeiska författare uttalat sig, bl. a. Ascherson & Graebner (34 pp. 719—720), Höppner (35), Fischer (31), Keller & Schlechter (32 p. 212) och Gsell (36), vilka auktorer liksom exempelvis Schur (37) ge ± utförliga beskrivningar.

mans med vilken vår typ ofta förekommer i Östergötland. — Bland exemplar insamlade av Gorton vid Örup i Skåne, föreligga under namn av »*O. incarnata* × *latifolia c. flor. alb.*» (VI. 1913, U!) sannolika hybrider mellan vår typ och *O. majalis*; ifrågavarande exemplar avvika nämligen från typisk var. *ochroleuca* genom bredare och rundare blad med största bredden ett gott stycke ovan basen samt genom betydligt större underläpp (c. 7 × 10 mm.), varjämte delar av blomman, åtminstone den pollinierna omgivande pungen, synas ha en svagt rosa anstrykning. — Från vissa lokaler på Gotland och i Skåne (Bårslöv) uppges *O. strictifolia* uppträda i alla möjliga färgformer. Då jag ej haft tillfälle besöka någon sådan lokal eller ens att granska vare sig levande eller pressade färgserier från en dylik, måste åt kommande forskningar — och åt forskare bosatta i lämplig trakt — överlämnas fastställandet av huruvida färgvariationen helt eller delvis beror på korsningar med var. *ochroleuca*. — Höppner (35) har från Rhenlandslokalen beskrivit korsningar mellan vår typ och såväl »*O. incarnatus* lus. *incarnatus*» som »*O. incarnatus* lus. *purpureus*», hos vilka hybrider läppen helt eller delvis behållit sin gula färg, varjämte Gsell (36) från Liechtenstein beskrivit hybriden »*O. incarnatus* × *ochroleucus*» under namnet *O. pedemontanus* Gsell.

I detta sammanhang må påpekas, att enstaka individ med halmgula blommor anträffats även av andra *O. strictifolia*-typer. Sålunda meddelar Pugsley (12 b p. 52): »In West Surrey similar straw-coloured concolorous flowers may be seen on individual plants growing with red-flowered examples considered to be var. *pulchella* Dr., which they match exactly in everything except colour.» Analogien med *O. sambucina* och dess bägge färgformer ligger också nära till hands, varför det ingalunda voro förvånande, om det till var. *ochroleuca* funnes en rödblommig parallellform. Pugsley (l. c.) framhåller emellertid, att en dylik ej synes vara känd; och i Sverige har ej heller någon typ anträffats, som kan betraktas som sådan. Om en dylik skulle finnas, bör dess blomfärg ej vara den vanliga ± violettröda (köttröda eller rosa) *strictifolia*-färgen utan en fylligare röd till purpurröd färg, jämförlig med den hos röd *O. sambucina* eller hos nyssnämnda var. *pulchella*, vilken beskrives som "bright reddish purple" (2 p. 579).

Tillfället må ock begagnas att peka på ett par andra typer av *latifolia*-gruppen, vilka föga uppmärksammats hos oss och vilka äro i största behov av utredning. Alla moderna florister äro eniga om att *O. strictifolia* undantagslöst har ofläckade blad, under det att samtliga övriga nordiska arter av gruppen ha dem normalt fläckade, även om fläckarna hos enstaka exemplar kunna vara urblekta eller helt saknas.

I de sydsvenska kalkkärren förekommer, som bekant, en art med på bägge sidorna starkt fläckade blad, *O. cruenta* O. F. Müll. Denna överensstämmer till utbredning och ekologi i allt väsentligt med *O. strictifolia* var. *ochroleuca* men har dessutom en vidsträckt utbredning i norra Sverige och är särskilt allmän i Jämtlands silurområde. Men även utanför de extremaste kalkområdena i Syd- och Mellansverige förekommer på sina håll en typ, som till habitus närmast erinrar om *O. strictifolia* och som i allmänhet etiketterats som *O. incarnata* men vars läpp är något större, spec. något bredare, och kanske något mindre hopvikt och vars blad på bägge sidor ha starkt framträdande fläckar, på översidan cirkelrunda och ofta 2—3 mm. i diam. men på undersidan mindre och oftast ± utdragna i bladets längdriktning För sistnämnda typ, som synes särskilt rikt företrädd i Närke och Uppland, har intet namn varit mig möjligt att finna i svensk floristisk litteratur. Att den skulle vara blott en modifikation av *O. cruenta*, synes föga sannolikt.

Vid ett besök sommaren 1943 inom det märkliga norduppländska kalkkärrområdet Mararna (Älvkarleby s:n) i avsikt att studera *O. Traunsteineri* (jfr 38) anträffade jag utom denna art även *O. strictifolia* (endast rödblommig) och en mig alldeles främmande typ, som habituellt kom den därstädes växande *O. strictifolia*-typen mycket nära, ehuru läppen var något bredare och något mindre tillbakavikt och bladen på bägge sidor bitvis hade svaga men tydliga, ytterst små, nästan punktformiga mörka fläckar i rader mellan nerverna. Denna typ synes tidigare ha helt undgått de nordiska floristernas uppmärksamhet.

Om det ytterligare tillägges, att *O. pseudocordigera* Neum. (= *O. Blyttii* Sóo) och *O. lapponica* Laest. ex Rchb. fil. äro ett par nordliga, ytterst ofullständigt kända former, vilkas för-

hållande till varandra och till *O. Traunsteineri* Saut. ännu är alldeles oklart (jfr 39) och att formerna av denna senare alltjämt äro lika outredda som dem av *O. strictifolia* och *O. cruenta*, torde önskvärdheten framstå tydlig, att de svenska floristerna ånyo ville ägna uppmärksamhet åt denna grupp och lägga sig vinn om hopbringandet av ett välkonserverat och representativt material. Det i våra offentliga museer förefintliga är alldeles otillräckligt och föga lämpat för närmare undersökningar, enär det till stor del behandlats med kokhett vatten, varma strykjärn el. dyl., varigenom såväl bladens eventuella fläckighet som blommornas färg och teckning försvunnit. Om stjälkar och knölar omsorgsfullt krossas med en knivsrygg el. dyl., låta dessa växter pressa sig på vanligt sätt men fordra täta ombyten med verkligt torrt papper. Än bättre kan bladens fläckighet och blommornas teckning bevaras, om avskurna blad och lösa blommor pressas för sig under iakttagande av att delar av olika individ ej böra blandas. Möjligheten att bevara blommans detaljer genom fotografering av levande exemplar (i svartvitt eller i färg) borde också flitigt utnyttjas samtidigt som de fotograferade exemplaren konserveras.

Lokalförteckning.[1]

Sverige.

SKÅNE.

Benestad: Örup, VI. 1914, A. Edv. Gorton (G!, s. n. *O. incarnata* × *latifolia*; una cum hybr.); d:o, 12. VI. 1915, Thorsten Sjövall (G!, s. n. *O. incarnata* × *latifolia*; una cum hybr.); d:o, 5. VI. 1921, A. Edv, Gorton (U!). — **Ö. Sönnarslöv:** Maltesholm, 12. VII. 1928, A. Lindquist (G!). — **Everöd:** mellan Lyngby och Mjö, kalkkärr, Th. Lange (in litt.). — **Trolle-Ljungby:** Gyetorps kalkkärr, Th. Lange (in litt.). — Landöns fiskeläge, extremrikkärr, 13. VI. 1944, Olof Andersson (in litt.; tills. m. åtskilliga, till storleken starkt luxurierande typer, intermediära till rödblommig *strictifolia*). — **St. Harrie:** Rinnebäck, extremrikkärr med dom. *Schoenus ferrugineus*, 3. VI. 1943, J. Hallberg (hb. ips.!). — **Bårslöv:** vid Nymölla, Ö. om landsvägen till Gantofta, extremrikkärr, 1942—43, Th. Lange (in litt.; »tillsammans med alla möjliga färgvarieteter»). — **Brunnby:** »Rydbergs mosse», VI. 1925. Henning Nilsson (hb. ips.!). — NÖ. om kyrkan, kalkkärr, Th. Lange (in litt.).

[1] Uppgifter ur Botaniska Notiser och Svensk Botanisk Tidskrift citeras här med BN och årtal resp. SBT och årgång.

ÖLAND.

Kastlösa: Rösslösa, strax S. om Borgbyborg-lokalen, i starkt tuvad kärräng, huvudsakligen *Sesleria*-äng, R. Sterner (in litt.). — **Mörbylånga:** V. om Borgby borg, 1853, M. M. Floderus (U!; BN 1854 p. 162, s. n. *O. incarnata* var. *albiflora*); Borgby borg, vid foten av landborgen, i starkt tuvad kärräng, huvudsakligen *Sesleria*-äng, R. Sterner (in litt.). — **Resmo:** 1870, P. A. Melin (U!); i diken, VII. 1874, T. Krok (S!, s. n. *O. incarnata—ochroleuca*?). — **Vickleby:** 16. VI. 1914, Alf. Ahlqvist (G!). — **Sandby:** alvarkärr S. om Skarpa Alby, i *Schoenus*-kärr, R. Sterner (in litt.). — **Torslunda:** Lenstad, »mosse», 25. VI. 1920, L. Lindquist (G!). — Ö. om landsvägen till Gårdby, mitt för Äpplerum, i *Carex Hostiana*-kärr, R. Sterner (in litt.). — 1 km. SÖ. om Kåtorp, i *Sesleria*-äng med enstaka *Schoenus ferrugineus*-tuvor, R. Sterner (in litt.). — 1 ½ km. S. om Tveta, i *Sesleria*-äng med enstaka *Schoenus ferrugineus*-tuvor, R. Sterner (in litt.). — **Algutsrum:** V. om Jordtorp, i ett *Carex Hostiana—Oederi*-kärr, R. Sterner (in litt.). — Mellan Gråborg och Tveta, VII. 1929, G. A. Westfeldt (hb. ips.!). — **Borgholm:** VI. 1880, Skg (S!). — **Alböke:** Petgärde träsk, R. Sterner (in litt.).

GOTLAND.

Vamlingbo: Bonsarve. kalkkärr, Th. Lange (in litt.). — **Fardhem:** Mästermyr. 1909, Th. Lange (in litt., »tillsammans med rödblommig»); [el. **Levede** el. **Silte** el. **Hemse**]: d:o, 1885, Th. A. Säterwall (S!); d:o, C. A. E. Lénström (BN 1888 p. 261, s. n. *O. angustifolia c. fl. alb.*). — **Stånga:** myrarna omkring Stånga slott, mycket vanlig, C. A. E. Lénström (BN 1888 p. 261, s. n. *O. angustifolia c. fl. alb.*). — **Fröjel:** 10. VI. 1911, R. Florin (S!). — E. Th. Fries (BN 1932 p. 104, s. n. *O. cruenta* f. *ochroleuca*) = Nymans, *Schoenus ferrugineus*-myr, 24. VI. 1927, E. Th. Fries (hb. ips.!). — **Klinte:** VI. 1861 [C. F. Nyman] (S!, una cum *f. fl. rubr.*). — Fuktäng vid prästgården, 21. VII. 1925, Bror Nilsson (S!). — Vid Mölner, kalkkärr, Th. Lange (in litt.). — **Hejde:** vid träsket, 15. VI. 1889, F. E. Alfvengren (S!). — **Väte:** VII. 1892, Rudolf Larsson (S!). — **Buttle:** E. Th. Fries (BN 1932 p. 104, s. n. *O. incarnata* f. *ochroleuca*) = Lindhammars myr, *Schoenus ferrugineus*-myr, E. Th. Fries (in litt.). — **Vänge:** Vänge myr, kalkkärr, Th. Lange (in litt.). — **Gothem:** Lina myr, kring Råby träsk, bland *Schoenus ferrugineus*, 8. VI. 1937, G. Sandberg (enl. muntl. meddelande; jfr 23 p. 292: »*O. incarnata* i rik färgväxling»; fig, 2 och 25). — Gothemsåns flodbädd nära utloppet, *Schoenus ferrugineus*-myr, VII. 1918, E. Th. Fries (hb. ips.!); Gothemsåns utlopp, kalkkärr, Th. Lange (in litt.). — **Roma:** Roma myr, 1849, K. J. Lönnroth (U!; una cum *f. fl. rubr.*);

d:o, 1897, Vilh. Strandberg (S!; una cum *f. fl. rubr.*). — **Visby stad:** Snäckgärdet, 1841, P. C. Afzelius (Hb. norm. VII: 66, s. n. *O. incarnata* var. *alba* Afz. fil.); d:o, 25. VI. 1842, C. Hartman (U!, s. n. *O. angustifolia* med hvita bl.) = »Wirby Hartman fil.!» (19 p. 52, s. n. *O. incarnata* a. *lanceata*. Specimina albiflora . . . stramineo-eburnea et luteola.); d:o, C. A. E. Lénström (BN 1888 p. 261, s. n. *O. angustifolia c. fl. alb.*) etc. — Nedom Galgberget, 30. VI. 1885, K. Johansson (U!). — Kalkkärr norrut, 26. VI. 1911, K. Johannson (U)). — **Visby s:n:** Kolens kvarn, 10. VI. 1910, The Svedberg (hb ips.!); d:o, *Schoenus ferrugineus*-kärr, V. 1920, E. Th. Fries (hb. ips.!); d:o, 6. VII. 1927, E. Th. Fries (G!, S!, U!); d:o, äng, 19. VIII. 1928, A. Nygren (U!). — **Västkinde:** E. Th. Fries (BN 1932 p. 104, s. n. *O. incarnata* f. *ochroleuca*) = Brissund, E. Th. Fries (in litt.). — Skälsö, kalkkärr, Th. Lange (in litt.). — **Lummelunda:** 1855, M. M. Floderus (U!); 27. VI. 1879, Sten Lewenhaupt (U!; una cum *f. fl. rubr.*); 27. VI. 1909, T. Erdmann (S!; una cum *f. fl. rubr.*); E. Th. Fries (BN 1932 p. 104, s. n. *O. incarnata* f. *ochroleuca*). — Lummelunds bruk, 17. VI. 1872, J. E. Zetterstedt (U!); d:o, VI. 1921, Nils Johnsson (G!; una cum *f. fl. rubr.*); d:o, E. Th. Fries (in litt.). — Strandkärr nedom Etebols, E. Th. Fries (in litt.). — **Stenkyrka:** E. Th. Fries (BN 1932 p. 104, s. n. *O. incarnata* f. *ochroleuca*) = Kvie, *Schoenus ferrugineus*-myr, E. Th. Fries (in litt.); Våthagen, 2. VII. 1914, K. Johansson (U!). — **Tingstäde:** vid Tingstäde träsk, nordöstra sidan, 25. VI. 1909, K. Johansson (S!, U!; una cum *f. fl. rubr.*); Ö. om träsket, *Schoenus ferrugineus*-kärr, 26. VI. 1923, E. Th. Fries (hb. ips.!). — **Othem:** E. Th. Fries (BN 1932 p. 104, s. n. *O. incarnata* f. *ochroleuca*) = Pussmyr, *Cladium*-myr, E. Th. Fries (in litt.).— **Lärbro:** in pratis, 1840, C. F. Nyman (U!) = »Gotland C. F. Nyman!» (19 p.52). — E. Th. Fries (BN 1932 p. 104, s. n. *O. incarnata* f. *ochroleuca*) = (nu uppodlad) myr Ö. om kyrkan, *Schoenus ferrugineus*-myr, E. Th. Fries (in litt.). — **Hangvar:** nära kyrkan, kalkkärr, Th. Lange (in litt.).

ÖSTERGÖTLAND.

Ödeshög: 1 km. S. om Sjöstorp, »*Schoenus ferrugineus*-societet i *Schoenion*-kärr», 1938, G. E. Du Rietz (27 p. 44). — **V. Tollstad:** Omberg, omkring Renstadsbäcken, B. Hesselman (SBT 32 p. 39, s. n. *O. incarnata* f. *ochroleuca*). — **Väversunda:** Dagsmosse, nordvästra kanten, A. F. Holmgren (BN 1851 p. 201, s. n. *O. incarnata*, »hvilken här i hvita blommor pryder hela sträckor») = »i Dagsmossen åt Väfversunda ängar och landsvägen» (l. c. p. 241, s. n. *O. incarnata* var. med hvita blommor); Dagsmosse, P. Dusén (40 p. 60, s. n. *O. incarnata* med hvita blommor; 18 p. 39); Dagsmosse, 6. VII. 1874, H. Vilh. Sjögren (S!). — Väversunda stor-

äng, 1845 (U!). — »Freberga hagar, Ekhaga hästhage, Djurkälla hage, kärret ovanför Eriksberg, *Schoenus*-kärret i Tyskeryds gärde, Tyskeryds kalvhage, Tyskeryds hage, Ostmossen, nedre Oxsumpen, nedre kärret i Postgårdsberget, kärr i Simonsgårdsberget», B. Hesselman (SBT 32 p. 39, s. n. *O. incarnata* f. *ochroleuca*. »Den senast blommande [av *O. strictifolia f. fl. rubr.*, var. *ochroleuca* och *O. cruenta*] är f. *ochroleuca*, vitgul eller vit, ofläckad, smalbladig och vanligen tämligen späd (dock även i högväxta exemplar), ymnig i kalkkärren och stundom den enda förekommande formen»). — Ekhaga hästhage, »*Schoenus ferrugineus*-societet i *Schoenion*-kärr», 1938, G. E. Du Rietz (27 p. 44). — Kalkkärr ovanför Eriksberg, 4. VI. 1943, J. A. Nannfeldt (n. 6449; U!). — **Rogslösa:** Borghamn, 1. VII. 1881, A. Wirén (S!, U!); ängar N. om Borghamn, B. Hesselman (SBT 32 p. 39, s. n. *O. incarnata* f. *ochroleuca*). — **Hagebyhöga:** »Hagebyhöge, Winnerstad, Vitfoten af Omberg, Holmgren!» (19 p. 52). — Öppna kärr vid torpet Sanden, Hj. Holmgren (BN 1843 p. 64, s. n. *O. incarnata* var. *alba*; jfr Kalén, BN 1842 p. 46: »*Orchis angustifolia* Koch både med röda och hvita blommor»); torpet Sanden i kärret, 1845, K. J. Lönnroth (U!); i kärr vid torpet Sanden, 12. VII. 1848, J. E. Zetterstedt (U!). — Medhamra, VII. 1860, N. A. Johansson (G!); kalkkärr nära Medhamra äng, 10. VII. 1853, J. E. Zetterstedt (U!). — Hageby Skattegårds kärräng, 1922, C. Fries (17 p. 78, s. n. *O. incarnatus* var. *ochroleucus*, foto.; p. 81: »röda eller vita ängsnycklar»). — **V. Stenby:** 29. VI. 1847 [Hj. Holmgren] (U!). — S. Fredberga vid Jerusalem, 1871, C. O. J. Hamnström (G!). — **Vinnerstad:** »på öfvergångsformationen [= silurformationen] såväl här som i grannsocknarna [d. v. s. Hagebyhöga och V. Stenby]», Hj. Holmgren (BN 1843 p. 56, s. n. *O. incarnata* var. *alba*; jfr BN 1841 p. 150: »allmänna i kärren och på sidlända ängar äro *Orchis latifolia* både med röda och hvita blommor . . .») = »Öfvergångstrakter såsom Vinnerstad, Hagebyhöga och V. Stenby socknar etc.», Hj. Holmgren (U!, s. n. *O. incarnata* var. *alba*); »Motalatrakten (Vinnerstad)», bland *Schoenus ferrugineus*, 25. VI. 1849, K. A. Holmgren (n. 1; S!) = »Östgötaslätten» [K. A. Holmgren] (n. 1; U!) etc. — I ett kärr mellan kyrkan och Sonnorp (S!). — I kärr vid Boren, 27. VI. 1863. H—m & L—s (S!). — **Kärna:** »in scaturiginosis et paludosis Jacobslunds mosse, copiosius», C. J. Wessén (16 p. 49, s. n. *O. latifolia* var. *floribus albis*); Värö mosse, VI. 1861, N. C. Kindberg (U!); d:o, 21. VI. 1920, Per H. Johansson (U!); Kärna mosse, 3. VII. 1904, C. Blom (G!); d:o, omedelbart S. om järnvägen, 19. VI. 1918, J. A. Nannfeldt (U!); mossen vid järnvägen, 16. VI. 1937, Henning Nilsson (hb. ips.!). — **Vreta kloster:** Sjögestad Postgård, 9. VII. 1915, Per H. Johansson (U!).

VÄSTERGÖTLAND.

Vartofta-Åsaka: O. Nordstedt (7 p. 245, s. n. *O. incarnata* var. *borealis ochroleuca*). — **Dimbo:** Elias Melin (7 p. 245, s. n. *O. incarnata* [typica] *ochroleuca*). — Lambevadskärret (c. 1 km. SSV. om kyrkbyn), *Schoenus*-kärr, N. Albertson (in litt.; »tillsammans med *O. strictifolia* med skära blr och ofläckade blad»). — **Åsle:** Svarttorp [= Svartarp], nära Dyängen, H. Witte (BN 1902 p. 280, s. n. *O. incarnata c. fl. alb.*); Gerumsberget, Svartarpskärret (c. 2 km. NNÖ. om Svartarps gård), *Schoenus ferrugineus*-samhälle, VII. 1941, N. Albertson (SBT 36 p. 88, s. n. *O. strictifolia* »den robusta, vitblommiga form, som anträffas i så gott som alla kalkkärr i trakten»); Gerumsberget, i kalkkärr nedom gården Klevan, 4. VII. 1932, J. A. O. Skårman (S!, U!; SBT 27 p. 386, s. n. *O. incarnatus* f. *ochroleucus*; »minst ett 20-tal individ sedda i juli 1932; märkligt nog saknas huvudarten med röd färg därstädes fullständigt»). — Varvsberget, Fårdala, i äng åt V., J. A. O. Skårman (SBT 27 p. 386, s. n. *O. incarnatus* f. *ochroleucus*). — **Falköping:** Hule mosse (c. 1 km. SV. om staden), 29. VI. 1935, A. Hillestrom (G!). — **Marka:** Mössebergs SÖ-sluttning, Bestorp, *Schoenus*-kärr, A. Hillestrom (sec. N. Albertson in litt.; una cum *O. cruenta*). — **Brunnhem:** Brunnhemsbergets Ö-sluttning, vid Smedsgården, *Schoenus*-kärr, 10. VII. 1943, O. Albertson (hb. ips.!). — **Borgunda:** Nolheden, *Schoenus*-kärret, 21. VI. 1941, N. Albertson (hb. ips.!). — **Högstena:** Plantaberget, kärr vid Stutagården, J. A. O. Skårman (SBT 27 p. 386, s. n. *O. incarnatus* f. *ochroleucus*). — Kärr vid Skogastorp, J. A. O. Skårman (SBT 27 p. 386, s. n. *O. incarnatus* f. *ochroleucus*); Skogastorp, kalkkärr, 9. VII. 1942, A. Hülphers (S!); d:o, *Schoenus*-kärret, 21. VI, 25. VI. & 1. VIII. 1941, N. Albertson (hb. ips.!) = Skogastorpkärret, *Schoenus*-kärr, N. Albertson (BN 1942 p. 87, s. n. *O. incarnata* vitblommig; una cum *O. cruenta*).

Danmark.

BORNHOLM.

Bodilsker »Kjøllergaards Mose», 1894, L. M. Neuman (BN 1896 p. 90, s. n. *O. incarnata* f. *ochroleuca*; BN 1909, s. n. *O. incarnata* var. *subextensa ochroleuca*).

SJÆLLAND.

»Lojet» Nord f. Grevensvænge pr. Næstved, VI. 1879, J. Nielsen (U!).

Storbritannien.[1]

Endast de av PUGSLEY publicerade fynden kunna anses säkra:

NORFOLK.

»In a fen near Diss» (12 a p. 125) samt en andra lokal (12 b p. 52).

Med hänsyn till förekomsten av andra gulvita former (12 b p. 52) måste andra uppgifter tagas med reservation. Påpekas må uppgifterna från SUSSEX: Aldworth (41) om *O. incarnata* »with purple, rose, and straw-yellow flowers» och från LEICESTERSHIRE och RUTLAND (42) om *O. incarnata* med blommor »flesh coloured, straw coloured, pale pink».

Frankrike.

Någon bestämd uppgift har jag ej kunnat anträffa, men ROUY (43) beskriver *O. incarnata* med »fleurs carnées ou ± blanches, très rar[t] jaunes». Med tanke på dess utbredning i Schweiz vore förekomster i franska Jura att vänta.

Tyskland.

RHEINLAND.

Nieder-Rhein, Kr. Neuss, Straberger Bruch (b. Uckrath), 18, V. 1918, H. HÖPPNER (Orchid. exs. II: 43, s. n. *O. incarnatus* var. *ochroleucus* f. *trifurcus* Rchb.; G!; 35 p. 270: »jetzt verschwunden, . . . wohl dem einzigen Standort in Rheinland und Westfalen»).

MECKLENBURG.

Sternberg, Cölpin (b. Criwitz), Rodenwalde (unweit Wittenburg), Krakow och Neubrandenburg im Wolfswinkel (20, 21).

BRANDENBURG.

Lychen Obersee, Neu-Ruppin, Trebbin Gütchendorf, Belzig Seedocke och Teupitzer Wiesen (44).

POMMERN.

Putbus, Wolgast, Trantow, Massow och Löcknitz (b. Stettin) (44, 45).

[1] I fråga om utomskandinaviska lokaler är förteckningen med naturnödvändighet mycket ofullständig, grundad som den är på exemplar i svenska herbarier och på lättillgänglig floristisk litteratur.

POSEN.

Meseritz, im Sumpfmoore, 12. VI. 1882, Th. Meyer (G!); Pakosch Netzewiesen (44).

BADEN.

Radolfzell Mindelsee (32 tab. 361 fig. 3).

WÜRTTEMBERG.

Någon speciell lokal är mig ej bekant men Bertsch (46) beskriver *O. incarnata* med blommor »rot od. weiss, selten blassgelb».

BAYERN.

Talrika lokaler (se exempelvis 19, 30, 45); Dachau, VI. 1914, Kurz (G!).

Lettland.

»Kemmern um Kangern-See» (51, s. n. *O. incarnata* flore flavo, det. Klinge) och västra Zemgale (52).

Estland.

Uppges av Lippmaa (50) förekomma i »Estonia inferior» och »Estonia maritima insularis» och vara kalkväxt.

Schweiz.

WAADT.

Villeneuve och »Les Rigoles zwischen Muraz und Vionnaz (32 tab. 362 fig. 2; 47).

AARGAU.

Hallwyler See (32 tab. 207 fig. 2).

ZÜRICH.

Hopern (b. Nänikon) (48).

SCHWYZ.

Mühlemoos (b. Buttikon) (47).

GRAUBÜNDEN.

»Zwischen Landquart und Maienfeld» (36 p. 9).

Liechtenstein.

Klein-Mels (32 tab. 361 fig. 1—2; 36 p. 9); Melser-Riet (5 p. 567).

Vorarlberg.

Frastanzer-Au (34 p. 720).

Tirol.

Nals (b. Meran) (34 p. 720).

Nieder-Österreich.

Moosbrunn (19, 37[1]); Sümpfe bei Moosbrunn, 180 m. s. m., 18. VI. 1896, A. Hayek (n. 2101, s. n. *O. incarnata* var. *foliosa* f. *ochroleuca*; G!).

Polen.

En allmän uppgift hos Hegi (33 b) är enda mig bekanta.

Ungern.

Sällsynt enligt Javorka (53).

Rumänien.

En allmän uppgift hos Hegi (33 b) är enda mig bekanta.

Summary.

Orchis strictifolia Opiz var. _ochroleuca_ (Boll) Hyl., an overlooked inhabitant of Swedish calcareous fens.

The said plant is shown not to be an albino form of typical *O. strictifolia*, for which it has as a rule been mistaken in Swedish floristic literature. Though albinos exist, they are very rare and no certain find is known from Sweden. A detailed report of the Swedish distribution of the var. *ochroleuca* is given (comp. fig. 1), to which a short review of its total distribution is appended. Our plant is in Sweden restricted to

[1] Lokalen för Schur's fynd (37) uppges felaktigt av Ascherson & Graebner (34 p. 720) som Semmering. Den ursprungliga *O. ochroleuca* Schur (49) från Siebenbürgen är skild bl. a. genom fläckade blad (jfr 12 b p. 52).

the most calcareous parts of the provinces of Scania (Skåne), Öland, Gotland, Östergötland, and Västergötland, where it inhabits only "extreme-rich-fens" (*sensu* Du Rietz, comp. 27, 28). Through its peculiar distribution and ecology it is well marked. Morphologically it is very uniform, but its morphological characters are rather faint. The colour of the flowers is a waxy white with the immaculate lips brighter yellow, in contrast to the white flowers of the albino form which often show a reddish tinge, at least in the pattern of the lips. The lips in our plant are more distinctly trifid (fig. 2) than they usually are in other types of *O. strictifolia*. — Hybrids with *O. majalis* have been found at Örup (in Scania), and such with *O. cruenta* were evidently seen in Östergötland by K. A. Holmgren, though no specimens are available.

In a short general account of the sect. *Dactylorchis* two Swedish types are mentioned which are closely affine to *O. strictifolia* but have spotted leaves. These types, which can not be united with *O. cruenta*, have hitherto escaped the notice of Swedish taxonomists and no name for them can be found in Swedish literature. It is furthermore pointed out that the diploid ($n = 20$) var. *Meyeri* Rchb. fil. of the otherwise tetraploid ($n = 40$) *O. maculata*, is synonymous to var. *obscura* Neum. and to *O. Fuchsii* Druce.

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The Institute of Physical Chemistry at the University of Uppsala.

Some Notes on its History and Activities.

By Sven Brohult and Nils Gralén.

The present Institute of Physical Chemistry at Uppsala is a young institution; in fact it was first taken into use in 1931. Its activities are, however, linked with the name of The Svedberg, and the work carried out there is, at least in many important respects, a continuation of the line of research followed by him and his collaborators during the two or three preceding decades. It is tempting to describe the whole background, but that would lead us far beyond the scope of the present article. It may be sufficient here to recollect that Svedberg, when he received a personal professorship of Physical Chemistry in 1912, had his laboratories in the Chemical In-

stitute built in 1904. There he made his first classical experiments in colloid chemistry, which already at that time made his name famous. There also the researches on the nature of liquid crystals and the fundamental photographic processes took place. A number of his young collaborators carried out the work for their theses there; some of them have contributed to the present volume.

In 1923 SVEDBERG received an invitation to U. S. A. as Visiting Professor at the University of Wisconsin, where he conducted a number of important investigations in colloid chemistry and, what is particularly important in this connection, obtained lasting impressions of American science and its efficient organisation. In many respects that year constituted a turning point in SVEDBERG's scientific career. At Madison he made, in collaboration with J. B. NICHOLS, his first successful experiments on the construction of a centrifuge with optical observation of the sedimentation. After returning home in 1924, he continued these experiments, which soon led to the construction of the first really efficient ultracentrifuges. A far-reaching programme was drawn up for the investigation of proteins by this and other new methods, which soon attracted scientists both from Sweden and abroad to collaborate with him. The new apparatus and the new people crowded the old laboratories; every corner was occupied, even cloak rooms and toilets had to house some of the equipment. The time was ripe for a new laboratory. The award of the Nobel Prize to SVEDBERG in 1926 gave further emphasis to the general opinion that something had to be done.

The plans for the building of a new institute began to take form in 1924, immediately after THE SVEDBERG's return from America. In 1926 the plans had progressed so far that SVEDBERG, in a memorandum of the 8th April to the Faculty of Mathematics and Natural Sciences in Uppsala, requested that the Faculty secure the inclusion in the University's parliamentary estimates for the budget year 1927—28 of a grant of 1.2 million Swedish crowns for the construction of a new physico-chemical laboratory. In this memorandum SVEDBERG stressed the need for increased space. The planned building was sketched and a list of the necessary equipment

of machinery and instruments was given. The request passed the relevant authorities with their recommendation and the requested sum was granted by the *Riksdag* in the beginning of 1927. Work on the new institute was commenced in August 1928.

In the planning of the present Institute of Physical Chemistry Svedberg joined forces with Yngve Björnståhl, one of the most prominent of his earlier pupils. The latter made very comprehensive preparations in the years 1925—28 and made a number of journeys in order to study scientific institutes both in Europe and America.

The building was constructed in the years 1928—31. It was built on to the existing Chemical Institute and connected with the latter by corridors. Certain facilities in the Chemical Institute, such as the lecture theatre and the library, are used by both institutes.

A detailed description of the Institute will not be given here, for Björnståhl performed that task in a work published in 1934, "The New Laboratory of Physical Chemistry at Uppsala University". Only a concise description of the Institute and the guiding principles in its equipment will be given.

The Institute has four storeys and a cellar. The building is remarkable for its efficiency; no unnecessary, pointless fittings are to be found. All spaces are employed in a rational manner. The electrical installation is quite complete, with a well-organised distributing system; in every room different kinds of current at several different voltages are available. Plants for high tension up to 200 kv are also installed. The rooms are well provided with other standard equipment, e. g. compressed air and water stills with extensive pipe systems. The rooms have been designed after the principle of easiest possible rearrangement for, and adaptation to different experimental requirements. Along the walls at table height run the Björnståhl shelves, i. e. shelves of about 20 cm. breadth with water, gas and compressed air outlets above and waste bowls let into the shelves. In front of the shelves are movable laboratory benches; in the walls and roof are sockets for the temporary mounting of apparatus and leads.

Svedberg had the fortune to find in Björnståhl a man

who approached the question of building and equipping the Institute with true scientific exactitude. It was a veritable life's work that BJÖRNSTÅHL accomplished, and his feat has justly aroused attention both in Sweden and abroad. Many institutes have been built after the model of the Institute of Physical Chemistry. BJÖRNSTÅHL's expert knowledge of scientific instruments was a great asset to the Institute, not only at the start but also later. When BJÖRNSTÅHL died in 1942, SVEDBERG wrote:

"BJÖRNSTÅHL had a pronounced theoretical gift. But despite this, or perhaps, in the deeper sense, precisely for this reason, he was interested in rational laboratory equipment and laboratory furnishings. In the planning of the present building of the Institute of Physical Chemistry at Uppsala, with its complicated and varied equipment of machines and instruments, BJÖRNSTÅHL displayed great activity. To BJÖRNSTÅHL falls the principal honour for the fact that such a satisfactory result was achieved. His skill was later made use of in the building of several other laboratories in this country, and his advice was requested for the solution of difficult laboratory problems in other countries. BJÖRNSTÅHL was rightly considered an almost infallible judge of such matters."

The Institute is well equipped with scientific instruments. It was considered already at the start that it should be furnished with a relatively complete equipment of generally used apparatus for research in physical and colloid chemistry and biochemistry. Several pieces of apparatus could be procured thanks to a grant of 50 000 dollars from the Rockefeller Foundation, made at the opening of the Institute, for the completion of its equipment. In addition, SVEDBERG has designed special instruments himself, and has stimulated his collaborators to similar work. In this way science has been given several valuable instruments, first built at the Institute of Physical Chemistry at Uppsala. Most of them have been built on relatively simple scientific principles, the successful application of which has been made possible by bringing the experimental methods to a high degree of perfection. In the course of time, the equipment, both of general and of special instruments, has been extended, and the Institute is now

The Svedberg at the control panel of the ultracentrifuge.
Photo copyright: K. W. Gullers.

certainly one of the best equipped physico-chemical institutes in the world.

As has been mentioned above, SVEDBERG had built an ultracentrifuge in the Chemical Institute. Shortly before the erection of the new institute this centrifuge was replaced by a new and more perfect type, soon followed by a second of similar construction. The two centrifuges were later found to

be insufficient for their increasing applications, and in 1938 a third instrument of the same type was built and installed. All three now run throughout the day and often at night.

A smaller type of ultracentrifuge, the motor-driven equilibrium centrifuge, was installed in four examples at the new Institute.

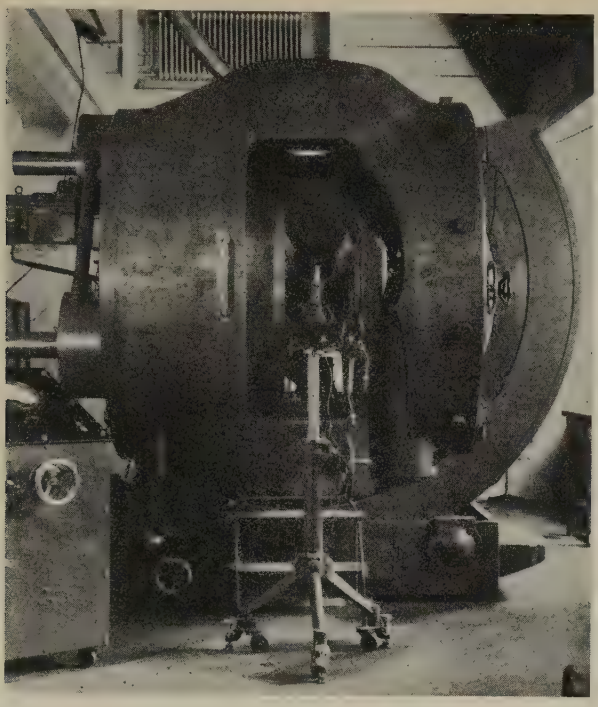
The measurement of diffusion was long considered to constitute one of the most difficult experimental problems. At this institute the diffusion technique has been developed, especially by O. Lamm, and used extensively. In the beginning only two apparatus were built, but nowadays seven are in use, several of them with arrangements for making two experiments simultaneously.

The electrophoresis technique was developed considerably by the work of A. Tiselius in the middle thirties, and several apparatus have been built here.

Among other special instruments developed in the Institute should be mentioned the arrangements for measuring streaming birefringence, and the apparatus for adsorption analysis, which has opened wide possibilities by rendering quantitative the old chromatographic method. Mention should also be made of a large electromagnet of maximum field strength 70,000 Oe, which was constructed by *ASEA* (designer L. Dreyfus) with the collaboration of Björnståhl.

Some generally used laboratory apparatus was already available when Svedberg's department moved from the Chemical Institute and was installed in the new institute. At the start, and later when necessary and possible, new apparatus has been obtained. Thus have been procured several spectrographs and monochromators for different wave-length ranges, microscopes, various mills, an automatically registering surface balance (built at the Institute), X-ray tubes and cameras for structural research, a neutron generator (also built at the Institute) for producing artificially radioactive elements, an air-driven Beams super-centrifuge, and recently an electron microscope.

The Institute has a first-class workshop, well provided with excellent machines. Svedberg realised at an early stage the great importance of the workshop in experimental research. A really high-grade instrument cannot be realised if there is

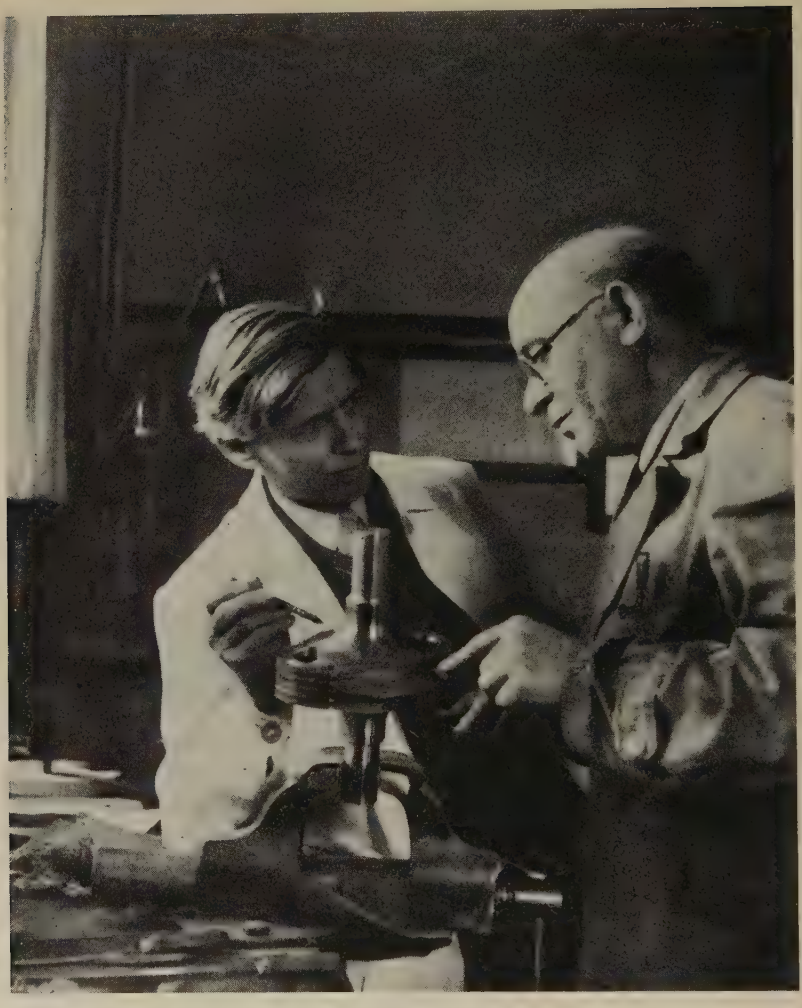


Electromagnet. Photo: L. Finn.

not intimate collaboration between the scientist and the mechanic. Such collaboration has always existed at the Institute of Physical Chemistry. The mechanic is just as often to be seen up in the laboratory acquainting himself thouroughly with the use of the apparatus, as the scientist appears down in the workshop to study the available technical possibilities.

The workshop at present employs ten first-class fine-mechanics. The head is Ivar Eriksson, who was already at the old institute when the first ultracentrifuge appeared. Before Eriksson came to Svedberg's laboratory, he had been employed in mechanical, electrical and optical workshops. His great skill and versatility have been an invaluable asset to the Institute with its great variety of work.

The workshop has become an increasingly important part of the Institute, for in many investigations the building of the apparatus is perhaps the most important factor. The result



A discussion in the workshop. Photo copyright: K. W. Gullers.

obtained depends as often on the work in the workshop as on that in the laboratory and at the desk.

The fact that the work at the Institute, with its sometimes complicated apparatus, progresses with so little friction, is due largely to the constant service provided by the workshop. If an apparatus is damaged, it can often be repaired very rapidly, thanks to the fact that the work is carried out by the mechanic or mechanics who have once partaken in its

construction. Repairs that would otherwise take several weeks or months can now be done in a few hours.

A great number of special apparatus, especially those named above, have been built in the Institute's workshop. Several of these have been made for scientific institutes abroad. Thus, out of four oil turbine ultracentrifuges, two went to England and two to America.

The calculating department. Photo copyright: K. W. Gullers.

The calculating department is a rather unusual feature for a chemical laboratory. It employs seven persons and takes charge of, among other things, the measurement of photographic plates, the plotting of curves, and above all the extensive calculating work connected with the numerical treatment of the experimental data. This work is carried out by specially trained personnel and is so effectively divided into different tempos that the results come forth as in a well-organised industry with moving-belt production.

The calculating department is of quite special value to foreign research workers and other guests, who are able to stay for only a short time at the Institute. These need not devote themselves to the — especially for a beginner — laborious calculating work, which is carried out more rapidly and efficiently by the trained personnel, but can direct their whole attention to their research problems.

The head of the calculating department, Evald Hellman, has been at the Institute since the beginning of the centrifuge

period. In him the research workers find an invaluable help when they are concerned with methods of calculation or in estimating the accuracy of different measurements.

The work at the Institute has been devoted mainly to the chemistry of large molecules. In the nineteen-twenties, when SVEDBERG began the work with the ultracentrifuge, the first objects studied were inorganic colloids, especially gold sols. In these experiments he collaborated especially with H. RINDE. Earlier BJÖRNSTÅHL had studied the accidental double refraction of colloids and he continued this work, especially on streaming birefringence, and extended his investigations to a large number of other substances.

SVEDBERG has had from his youth a deep interest in biology (in the choice of his course at the University he hesitated between botany and chemistry). The research programme in protein chemistry already referred to above thus had deep roots in SVEDBERG's mind. Haemoglobin was the first protein studied in the ultracentrifuge. It was found, rather astonishingly at that time, that this protein was monodisperse, i. e. uniform in molecular size. The proteins presented a particularly fruitful new field for the ultracentrifuge, and during the following years proteins were the main subject of research at the Institute. Several of them, especially those which are in solution in their native state, were found to be monodisperse like the haemoglobin. From the point of view of the experimental technique it was particularly fortunate that the ultracentrifuge was used at this early stage on monodisperse systems of relatively symmetrical molecules. The polydisperse systems, and the filamentous molecules (e. g. cellulose and its derivatives) give much more complicated phenomena in sedimentation experiments. The monodisperse proteins formed extremely valuable test materials during a period when a number of great technical difficulties in the construction and in the method itself had to be surmounted. Much attention was paid to improvements in the optical observation methods; here the "scale method" of LAMM (1928) was the most remarkable advance.

One of the first classes of proteins studied was that of the respiratory blood pigments, i. e. haemoglobins, haemocyanins, erythrocruorins, and haemerythrins. The sera of mammalia

were studied simultaneously, first by P. v. Mutzenbecher, later by A. S. McFarlane and K. O. Pedersen. Another prominent worker in the field of blood pigments and sera was G. S. Adair. Vegetable proteins, especially seed proteins, have also been investigated by Svedberg in cooperation with Laura Krejci and O. Quensel and others, and by A. G. McCalla. Among the workers in this sphere should also be mentioned J. W. Williams, who had already collaborated with Svedberg in Madison in 1923 and afterwards worked at the Uppsala institute in 1934—35.

All these works have been described by Svedberg and Pedersen in their monograph on "The Ultracentrifuge" (Oxford 1940, also published in German, Dresden and Leipzig 1940). This book gives a very complete review of the ultracentrifuge, its history, development, technique and use, and the results obtained with its aid.

The protein studies gave the work at the Institute a biochemical and even medical trend. Enzymes were studied by R. Kekwick, J. B. Sumner, H. Theorell and others, antibodies by M. Heidelberger, Pedersen and Tiselius. The latter two have also collaborated with Florence B. Seibert on tuberculin and with a number of Swedish and foreign investigators on various biochemical and serological problems. A great stimulus was given to the biochemical research when in 1938 a new chair of biochemistry could be established thanks to a gift of 500 000 Swedish crowns to the University by Major Herbert Jacobsson and Mrs. Karin Jacobsson, née Broström, of Gothenburg. Tiselius was to become the first occupant of this chair and received his appointment in May 1938. Svedberg, on whose initiative the professorship had been established, generously offered accommodation and equipment for the extended biochemical research which was to follow.

In recent years the study of viruses has been taken up. An intensive investigation of poliomyelitis virus has been performed by S. Gard.

From the inauguration of the Institute until 1939 or 1940 many foreigners were working guests. Svedberg's name and the famous experimental facilities of his institute attracted scientists from many countries. It sometimes happened that

the foreign workers were in the majority. The countries that have been represented are: Australia, Belgium, Canada, Czechoslovakia, Denmark, Finland, Germany, Great Britain, Holland, Italy, Japan, Poland, Roumania, South Africa, Switzerland and U. S. A. In this connection should be mentioned the financial assistance given to the Institute from its start by the Rockefeller Foundation. A large number of the visitors have been Rockefeller fellows. Several Swedish foundations have also given financial assistance to the work at the Institute. Regular contributions have been made by: "Thérèse och Johan Anderssons Minne", "Gustav V:s 80-årsfond", "Nationalföreningen mot tuberkulos", "Nobelfonden", "Knut och Alice Wallenbergs Stiftelse" and "Wenner-Grenska Samfundet".

The study of large molecules other than the proteins started at an early stage. As mentioned above, the filamentous molecules offer greater difficulties to the ultracentrifuge worker. The pioneers in this field of research were the Americans E. O. Kraemer and J. B. Nichols. Here should also be mentioned A. J. Stamm, who was the first to study cellulose in the centrifuge, and the Swiss R. Signer, who studied polystyrene and cellulose derivatives during several visits to Uppsala. His pupil H. Mosimann has continued his work. Later, this field of research has gained a widened interest. During the last years there has also been a tendency towards the study of high-molecular compounds in the solid state, i. e. by X-rays, electron microscope etc. These methods have attracted increasing interest especially in the study of technically important substances, e. g. cellulose and synthetic resins.

Many Swedish industries have sought contact with Svedberg, especially from 1937 onwards. He did not hesitate, but entered into cooperation with the industries, and this cooperation has been of great advantage both to science and technology. Especially during the period of isolation from the West which Sweden has suffered since 1940, cooperation with industry has been enlarged. The cellulose, rayon fibre, fat and soap, drug, brewing, sugar, photographical, and synthetic resin industries have all been, and still are, in cooperation with Svedberg and his Institute. The investigations made for industry have been within the bounds of the research pro-

Rubber mill in the corridor. Photo: L. Finn.

gramme of the Institute, the physical chemistry of high-molecular compounds, colloid chemistry and biochemistry, and most of them have been intimately connected with earlier work of Svedberg and his co-workers. The researches have mostly been of a purely scientific nature, but investigations of more direct technical interest have also been performed. Several publications have appeared concerning these investigations.

Among the industrial researches should be specially mentioned the work on synthetic rubber. Sweden's lack of natural rubber during the war made it necessary to work out methods for the production of synthetic substitutes, and Svedberg opened his institute for experiments on the production of neoprene. A very large part of the work at the Institute was

devoted to this task and the methods were worked out on different scales, from the laboratory experiment to the complete small scale rubber mill, which was built in one of the corridors. Parallel to this work, a purely scientific study of the properties of rubber was commenced. Most of the engineering work has now been transferred to the Swedish Rubber Research Institute at Uppsala, still under SVEDBERG's supervision. Based on experience and results gained at Uppsala, a factory has been built at Ljungaverk for the production of neoprene on a large scale, and a second is planned at Stockvik. Rubber still claims great scientific interest at the "mother institute".

As has been mentioned before, THE SVEDBERG's professorship is personal. Personal professorships in general provide partial exemption from the obligation to give lectures and partake in lower tuition. This applies also in SVEDBERG's case. He has thus been able to devote himself to research and the planning of future work, more undisturbed than many of his colleagues.

His lectures are, however, very stimulating, and usually deal with topical problems beyond the research programme of the Institute. He devotes much time and labour to the preparation of these lectures, always trying to refer to the original publications, avoiding second-hand information, and including the most recent facts from newly arrived scientific journals.

THE SVEDBERG has had many co-workers, both Swedes and foreigners. He has always been able to place the right man in the right place. Those concerned have sometimes perhaps not realised, until they have worked for several years, how rightly they have been judged by their teacher.

Work at the Institute of Physical Chemistry is principally devoted, as may be realised from the foregoing account, to the study of large molecules. Since these include very important and sometimes very different groups of substances, such as proteins, viruses, cellulose and plastics, it will be understood that the research problems are extremely varied and make great demands on the Head of the Institute. One hour he may be involved in medical discussions concerning some biologically active protein which is to be investigated,

the next hour the discussion may regard the molecular properties that determine the technical utility of a plastic. This ever-changing work must have been satisfying to THE SVEDBERG, who has always considered narrow-minded specialisation to be an abomination.

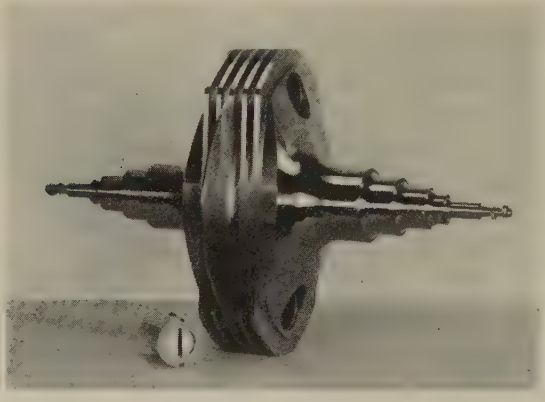
The idea of collaboration has always been popular at the Institute and team-work has perhaps occurred more frequently here than at other institutes in Sweden. At the same time SVEDBERG has always required of his collaborators that they must be able to work independently. This has been especially apparent in the case of doctoral theses.

The Institute of Physical Chemistry now has a staff of about one hundred. It is due largely to SVEDBERG's talent for organisation that the work proceeds as efficiently and frictionlessly as it does. From industry SVEDBERG has borrowed the principle of plentiful technical assistance for science. There is at least one technical assistant for each research worker; there is a well-equipped workshop where anyone can have his apparatus built, and there is a special calculating room with several assistants for the lengthy calculation of the experimental data.

Scientific research should be free, and this has been the guiding principle at the Institute. No undue conditions should be imposed on free research and no irrelevant obstacles should hinder the search for truth. Nor may the boundaries between the different branches of science provide insurmountable barriers. Science is universal, and not only the various branches of chemistry have been fostered within the walls of the Institute, but, when necessary, investigations have extended into the spheres of physics, mathematics, botany, zoology, medicine, geology and other sciences.

The intimate collaboration with industry has been advantageous both to industry and to science. THE SVEDBERG has contributed in a very high degree to the introduction of free unprejudiced science into Swedish industry; his great achievement here can scarcely be overestimated. On the other hand, purely industrial problems have opened new paths to science and have given impulses to the solution of purely scientific problems.

The Institute of Physical Chemistry at Uppsala has acquired world-wide fame. It has even served as a model for the organisation of scientific work in physical chemistry and other fields of science. The great work of SVEDBERG is intimately associated with the Institute, which has been an excellent instrument for him and his collaborators. Science has been brought forward in a manner that has received sympathy and appreciation, not only by men of science, but in far wider circles.



Ultracentrifuge rotor and cell.

Manuscript received June 3rd, 1944.

Research and Progress in the Textile Industry.

By Alex. Engblom.

Just as in other spheres of technical research, the problems of textile technology may be classed under two principal headings: fundamental and applied research, or, to use other terms, basic and directed research.

The former is of purely scientific character, works with distant aims and may in general be said to be concerned with the solution of more fundamental problems. Directed research has tasks of a more practical nature in that it seeks principally to solve problems directly connected with the different processes of production. The biochemical structure of cotton fibres may be taken as an example of a subject for basic research; the statistical distribution of fibre lengths in a certain type of cotton and its influence on the spinning properties or strength of the yarn is an equally typical subject for directed research.

The above classification is, however, more or less arbitrary. The boundary between basic and directed research is not sharply defined but rather diffuse, so that there is often a certain doubt as to whether a problem shall be considered to come under one or the other group.

Basic Textile Research as a Part of the Science of Macromolecular Materials.

Basic textile research belongs principally to that part of science which deals with macromolecular substances. These include not only the basic substances of fibrous materials, cellulose, keratin and fibroin, but the greater part of the materials used in the refining of the raw materials of textiles such as starch, dyestuffs, artificial resins, impregnation media

etc. The solutions of these substances are of a distinctly colloidal character and it is to the credit of modern colloid chemistry and the deeper insight this has provided into the physical and chemical properties of large molecules that textile research has been able to make such great conquests.

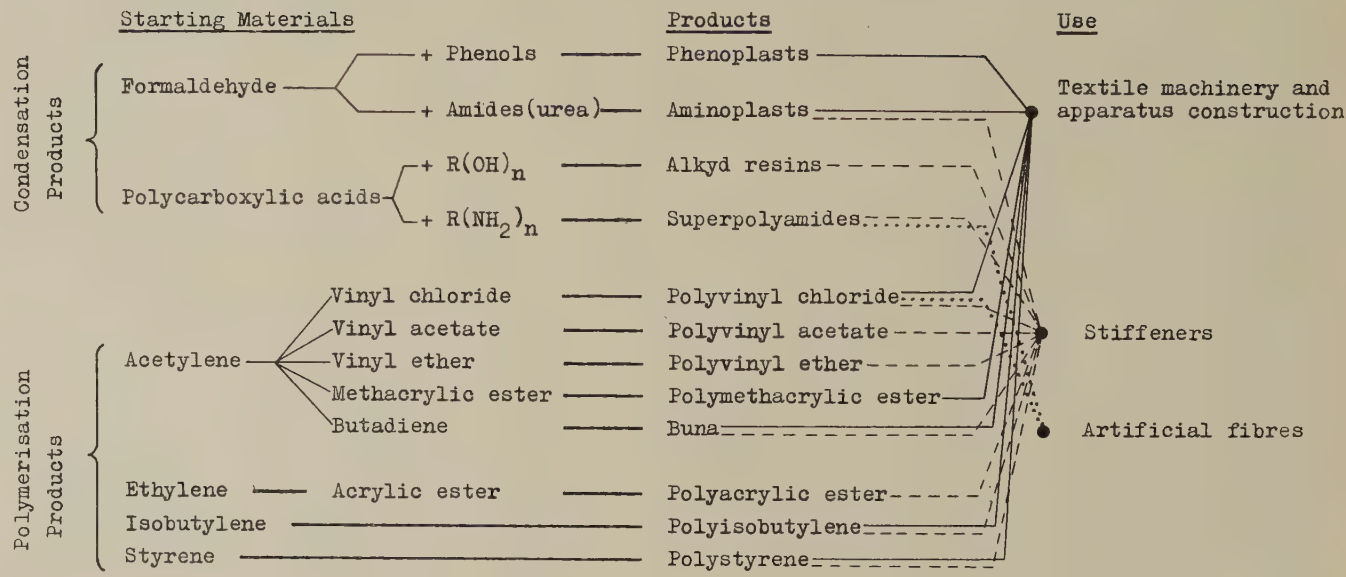
Space does not permit a detailed account of the interesting results achieved in this sphere. Only a few examples will be given of what has been published in recent years.

With the help of the electron microscope greater light has recently been thrown on the morphology and histology of fibrous materials. Thus the German workers Hess (1), Eisenhut and Kuhn have clearly demonstrated the difference between the sub-microscopic structures of native cellulose fibres and artificial fibres made from cellulose. The native fibres consist of bundles of elementary fibrils which are bound together by an outer skin or mantle. The artificial fibres, however, lack this biostructure. Hess has shown that it is this fibrillose structure that gives the native fibre its superiority over the artificial fibre with respect to durability. In the manufacture of artificial silk this result is of the greatest importance. If cellulose could be won from wood in such a manner that its fibrillose structure was not too seriously damaged, the durability of the artificial fibres would more nearly equal that of the native fibres. Schmieder, Gundermann and Krombach (2) have established an analogous fibrillose structure in the case of wool fibres. Their electron-microscopical photographs confirm earlier theories that wool fibrils consist of networks of sub-fibrils.

The fundamental chemical research in the sphere of high-molecular substances has already made many valuable contributions to the textile industry. The revolutionary discovery by the American Carothers of the purely synthetic polyamide fibre *nylon* opens wide prospects for textile research, just as does the German *perlon* fibre. Another new fibrous material is the *Pe-Ce* fibre of *I. G. Farbenindustrie*, which, by virtue of its power of resisting chemical action, has become an important material for technical spun goods.

Both the *nylon* and the *Pe-Ce* fibres belong to the large group of macromolecular materials known as plastics or ar-

Synthetic Polymers in the Textile Industry.



From "Kunststoffe in der Textilindustrie" by Dr. G. SCHWEN, Ludwigshafen am Rhein.
Melliand Textilberichte **23** (1942) Part 1.

tificial resins. Condensation products and polymers of this kind have found wide application in the sphere of textiles (see table). The possibility of varying the properties to meet requirements has brought forth materials for the most diverse purposes. Uncreasable fabrics, washable stiffeners and binding media for pigments in printed textiles are examples of the uses of artificial resins in the improvement of textiles.

The study of the colloidal phenomena that occur in the refining of textile materials have led to the discovery of an incalculable number of new expedients. The capillary-active colloidal electrolytes, soaps and detergents, have especially been the objects of research. The modern textile industry uses, instead of only soap and Turkey red oil, fatty alcohol sulphonates, the condensation products of fatty acids and proteins, sulphonic acids, sulphonium and ammonium bases. Whether these show anionic or cationic activity, it is a characteristic of all of them that they are strongly surface active and are insensitive to lime and acid. The deficiencies of soap in this connection have thus been eliminated.

Nüsslein (3) has even succeeded in preparing wholly synthetic washing media, quite free from fats. These also lack electrolytically dissociating groups in their molecules. Water-solubility is achieved by means of electrically neutral hydrophilic groups, for example accumulations of ether groups. These polyether-alcohols are thus not ionogenic and are practically insensitive to acids, alkalis and metallic salts.

The collaboration between science and technology has been very fruitful also in other branches of textile technique. Varieties of starch and gums which have played an important part in dressing and textile printing have found competitors in cellulose derivatives and polymerisation products. Of the former, fully adequate products, the glycol ethers, are made in this country.

Just before the outbreak of war the Americans Dubeau, MacMahon and Vincent (4) succeeded in the commercial preparation of sodium chlorite. In this the textile industry has acquired a valuable new bleaching medium, which, in contrast to those used at present, bleaches without destroying the cellulose.

Even such a time-honoured material as ultramarine, laundry blue, has been obliged to make way for more practical products. Fluorescent substances that emit blue light compensate much more effectively the yellowish tone of white textiles.

The examples provided here represent only a few of the results gained by basic textile research. The tremendous development of the last twenty years in the sphere of textiles is due entirely to the pioneering investigations carried out in research laboratories. Fortunately the textile chemistry of today boasts an ever-increasing number of research workers.

Abroad the institutes for textile research have produced in recent years a number of prominent scientists. Of the more prominent names we may mention Astbury, Haworth, Hess and Staudinger, whose results have been of inestimable value in the clarification of the fine structure of fibrous materials. The most prominent contributors to refining technique have been Bartell, Freundlich, McBain and Nüsslein. The colloidal research performed by these men in connection with surface active materials have had a very beneficial influence upon textile-chemical technology. Further noteworthy workers are Elöd, Schramek and Neale, whose exhaustive investigations of the influence on the taking up of dyestuffs of temperature, hydrogen ion concentration and added salts have been of decisive influence in dyeing technique.

In this country we have The Svedberg, whose work has been especially important in the study of high-molecular substances. As early as the beginning of the century he was one of the founders of colloid chemistry. In the nineteen-twenties his reputation became widespread, and ever since his institute has been a centre of high-molecular research, not only for Sweden but the whole world. During the last decade Svedberg has been in intimate contact with divers industries, including the textile industry, and he has been one of the prominent figures in the development of contacts between industry and scientific research. He has worked that the eyes of industrialists might be opened to the importance of fundamental research for industrial technique, and his contribution in this sphere cannot be overestimated.

Directed Textile Research.

The textile industry is extended over a large number of branches. For this reason directed textile research has great scope and variety. It lies in the nature of the thing, however, that each individual problem often has only a limited range.

Work on such problems has naturally been done throughout the world, both within industrial enterprises and at various more or less official institutions. Much has been published in the technical presses of all countries, especially in recent years. Much also has remained within the enterprises as trade secrets. It would be too great a task to review the directed research as documented in the technical journals. Some indications may, however, be given of the work carried out at the Textile Institute in Borås and at the State Testing Station.

The greater part of the investigations at the Textile Institute have been made on behalf of industrial enterprises, who have handed over many technical problems which they have not had the opportunities or resources to deal with themselves. Such investigations include:

The relationship between softening and spinnability in cell-wool.

The influence of the doubling twist on the strength of worsted yarns.

Investigation of the cohering power of cell-wool of the cotton type.

Comparative investigation of the strengths of cell-wool yarns with fibres of different lengths.

Variations in the thread tension in the ring spinning machine and their equalisation with the aid of revolution regulation.

Method for the predetermination of the spinnability of woollen materials.

Preparation of the most suitable yarns for machine-gun belts.

Investigation of the most suitable fibre length for cell-wool intended for admixture with cotton of a given type.

The relation between the cohering powers of differently finished cell-wools and the strengths of yarns made from these.

The influence of the spinning oil on the spinnability of wool fibre.

The specific strength of a fabric and its practical significance.

The influence of different washing media on the strength of fabrics.

As a consequence of the private nature of the investigations it has unfortunately been allowed to publish the results only in exceptional cases. A number of investigations have, however, been carried out on initiative from within the Institute. Thus Stig Kjellstrand has carried out investigations regarding the relationship between the tearing and breaking strengths of fabrics (5), the practical significance of the specific strengths of materials (6), the influence of weave and construction on the wearing properties of blue cloths etc.

Grants for research have come to the Institute partly from non-industrial quarters. Thus in 1936 Kjellstrand and Stig Löfgren received small research grants from *IVA*, the Royal Swedish Institute for Engineering Research. The former's work concerned "The Mechanical Properties of Wool Fibres" and the latter's "The Influence of Early and Late Parallelisation in the Spinning of Cotton and Cell-Wool." In the last mentioned research a problem was treated which had been of importance *inter alia* in the rationalisation of the cotton industry. The results of the two investigations are published in *IVA* Bulletin (7).

These grants were not, of course, intended to cover the costs of the investigations, but for the recipients they meant encouragement and an expression of appreciation for the newly founded textile research in Sweden.

In 1938 *IVA* awarded further research grants to the same persons. This time the investigations could be planned on a considerably wider basis and have not yet been fully completed. Kjellstrand has appreciably extended his work on the properties of wool fibres.

In his latest research Löfgren has taken up a problem which lies on the border between fundamental and applied textile research. The work is entitled "The Relation between the Form of the Staple Diagram and the Physical Properties of the Yarn and the Fabric." More extensive investigations can scarcely have been carried out earlier concerning the in-

fluence of the dimensions of fibres on, for example, the evenness of strands and yarns, the unbroken lengths and elasticities of yarns, the strengths, elasticities, wearing properties and porosities of the completed fabrics etc.

It is true that some of the above properties have been the object of research, but native fibres, usually cotton, have been used as material. With such a material it is practically impossible to vary one dimension at a time, e. g. the fibre length, and to keep all other properties unaltered. Egyptian cotton, for example, has a higher average fibre length than the American material, but also a higher degree of fineness in the fibres and a greater specific strength. Thus, by investigations of these two materials, it is impossible to determine the influence of the fibre length and its distribution on the properties of a product.

In the investigation in question artificial fibres have been used as experimental material. These were made in different lengths but under otherwise identical conditions. By mixing the different varieties in definite proportions a number of spinning mixtures with different staple diagrams were obtained.

In the case of yarns, investigations have been made as to how the form of the staple diagram affects the unbroken length and the elasticity. In order to obtain a complete picture of this relationship it has been necessary to work with a number of twist values on both sides of the so-called critical twist number.

Finally, yarns made from the different spinning mixtures have been worked up to fabrics which have been subjected to detailed investigations with regard to their breaking strength and wearing resistance, elasticity and porosity. The wearing resistance has been studied in especial detail by the construction of wearing series for each of the samples under test.

It is apparently the intention to complement this extensive investigation at the Textile Institute with a new programme concerning the fibre fineness and its influence on the above-mentioned properties of half and wholly finished products.

A number of investigations have also been carried out at the State Testing Station in Stockholm. Of these we may mention:

The chemical properties and composition of cotton.

Physical methods for the testing of textile fibres and products.

Determination of the strength characteristics of yarns.

The distinctions between flax and hemp fibres.

Sunn-hemp and New Zealand flax.

Methods for the distinction between mercerised and unmercerised cotton.

The antifading properties of wool dyed with vegetable pigments.

Investigations on the effect of washing media on cotton and linen fabrics.

The effects of different hard waters on the reduction of the strength of fabrics in mechanical laundering and on the cost of the latter.

In the last-named sphere, that of laundry research, a valuable contribution has been made by the Society for Rational Laundering at the *IVA*.

Finally we may recall the directed textile-chemical research which has been carried out for years within the private industrial concerns. At least where the larger enterprises are concerned, an often very well-equipped laboratory now constitutes an important part of the installation.

The Historical Development of Textile Research.

The selection given here from the successes of textile research is enough to show the extensive and thorough work which has been carried out (8). Naturally the work has had to be subjected to a certain somewhat rigid organisation, and it may not be out of place to give a survey, however brief, of how this organisation is performed.

Textile research abroad has gone hand in hand with the corresponding activity in other technical spheres. The research received its initial impulse from the experiences gained during and after the World War. In many circles the importance was realised of increasing the yields of technical processes as far as was possible. The shortages of important raw materials necessitated the search for substitutes. Even if many of the

results lost in value when conditions became more normal, the attitude towards research was altered and the need for it was understood.

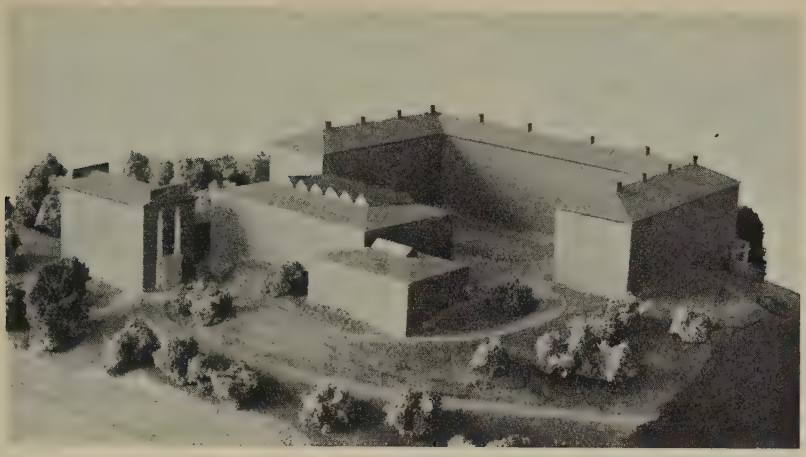
In England, as in the majority of other countries, research is carried out on three fronts: at the universities, through certain organisations subordinated to the Government and within the industries themselves. These three spheres of activity are not, however, mutually independent. University research is to a large extent dependent upon subsidies from the Government and from industrialists. On the other hand, a large part of the research at Government institutions and within the industries is in the hands of university teachers. Finally, state and industrial research are intimately connected, especially through the so-called research associations.

Textile research in Germany was largely initiated in the period commencing with the World War, even if certain scientists had already contributed to the development of textile industry. The magnificent development of textile research expressed in the many "Forschungsstellen" affiliated to the higher textile educational establishments is, however, only about twenty years old. These institutes are the bearers of contemporary textile research in Germany.

An intimate collaboration of research and industry has always been maintained in Germany. An unbroken contact also exists between the technical universities and the institutes for directed research. The collaboration between the Technische Hochschule in Stuttgart and the Institute in Reutlingen is a typical example.

America has been justly called "the land of great opportunities". This epithet is not least merited where textile research is concerned. Even though it may perhaps be said that technical research there became purposeful and comprehensive about ten years after the corresponding development occurred in Europe, results of great value have already been obtained thanks to the country's enormous resources and a favourable attitude towards the research idea.

In France, Holland, Belgium and Czechoslovakia the importance of broadly planned textile research has been realised in the last decades, even if this work has stagnated during



The Textile Research Institute at Chalmers University of Technology (photograph from a model). The Institute occupies the two central buildings; of these only the larger will be constructed in the beginning.

the war. It may be confidently expected that, after the conclusion of peace, these countries will take up their research again and render their contribution to an international advance in textile technology.

In comparison with the development in other countries, Sweden's contribution to textile research appears rather modest. Textile research in the modern meaning of the term would appear to have first been brought under general discussion at a series of lectures on textile matters arranged by *IVA* in Borås from 2nd to 4th March 1922. The programme was as follows:

Mr. A. F. Enström: "The Importance of Technical Progress to Industry."

Mr. H. Lundberg: "Some Modern Views on Industrial Steam Installations."

Mr. M. Lindhagen: "Heat-Utilising Apparatus in the Textile Industry."

Mr. H. Lundberg: "The Regulation of Fuel and Heat Consumption."

Mr. A. Engblom: "The Textile Industry and Technological Research."

Discussions arose in textile-industrial circles both in Borås

and Norrköping, where the importance was emphasised of a collaboration between *IVA* and the Swedish textile industry and of an extension of the weaving schools in Borås and Norrköping, so that they might give fuller and more thorough tuition in textile technology. Eventually the two schools were extended and became the Textile Institute in Borås and Lenning's Institute for Textile Technology in Norrköping. Both these educational establishments have proved capable of fulfilling the demands made on them. It should also be mentioned that a course in textile technology has been instituted at the Technical School in Borås. The students who pass through this course have an opportunity to improve their knowledge in a special one-year course, which is part of the programme of the Textile Institute.

The Present Situation in Sweden.

While directed textile research has come into being in Sweden in recent years, it must be admitted that it has not yet been possible to develop the fundamental research in the same field to any great extent. The only institution in the country where such research has taken place would appear to be the Institute of Physical Chemistry in Uppsala. The greater part of the relevant investigations undertaken there lie in the sphere of cellulose chemistry and the properties of cellulose fibres. It is therefore with gratitude that we record that fundamental textile research first appeared in this country under the supervision of The Svedberg.

The question of basic textile research now appears in quite a new light owing to the *Riksdag's* decision in 1943 to establish the Swedish Textile Research Institute in connection with Chalmers University of Technology. The proposal that led to this decision was made by the committee of inquiry into the organisation of scientific research under the chairmanship of Director-General G. Malm.

In its pronouncement concerning the Institute the committee states: "It is important that the scheme be not limited to the establishment of a central industrial laboratory for the solution of occasional difficulties in manufacture, nor to the crea-

Lenning's Institute for Textile Technology, Norrköping. Exterior.

tion of an institute on purely theoretical lines for the cultivation of the sciences, cut off from the developments in technique. Instead lines of work must be sought which facilitate in a natural manner the development of the conquests of theoretical scientific research by directed industrial research, to provide results applicable in practice to the satisfaction of the consumer's needs."

The tasks awaiting the Textile Research Institute extend over a wide range. It may be hoped, for example, that it will take up the great complex of problems mentioned at the beginning of this article. A first class equipment, satisfying the requirements of pure science and industrial practice, will be available in the near future for the solution of these problems.

The fact that the idea of a textile research institute has now been realised is due partly to state subsidies for the building and for certain annual expenses and partly to the generosity displayed by the textile and clothing industries. Industry has undertaken to meet the costs of machinery, apparatus and other equipment for the institute and also to cover the running expenses, the material etc. For this purpose a special foundation, "Svensk Textilforskning", has been founded with Mr. Axel Bergengren as chairman.

A condition perhaps more important than any other appears to be that the Textile Research Institute acquires, from the very beginning, personal contact with the institution where

fundamental textile research has already been commenced. That this will be realised is guaranteed by the appointment of one of Svedberg's pupils, Dr. Nils Gralén, as Head of the Institute. The doctoral thesis that Gralén has recently published (9) adds to the evidence that he is the right man to deal with the great mass of problems which await their solution.

It is quite natural that the greater part of the directed research is performed, as before, at the textile institutes in Borås and Norrköping. The Textile Institute in Borås was equipped, from its foundation in 1936, in such a manner that problems in directed research could be dealt with without delay. This intention has been carried out, as has been indicated above. As regards Lenning's Institute for Textile Technology in Norrköping, the building of an annex has recently been completed there, where, among other things, a large research laboratory will be installed. The Institute thus acquires greatly increased possibilities for the execution of textile research, all the more as industrial enterprises in Norrköping and other interested parties have contributed a sum of nearly 400 000 crowns to meet the costs of directed research over a five-year period.

In order to obtain results whatsoever in the Swedish textile research, it is necessary that adequately trained personnel with sufficient scientific capacity are available. The lack of such persons has hitherto constituted a drag upon textile research in Sweden.

As is well known, however, the experts appointed for the organisation of higher technical education proposed in their report certain measures for the introduction of education in textile matters at the universities. Even if this proposal must be considered as a minimum, it implies an essential step forward.

The Necessity of Continued Efforts.

As has been indicated above, comprehensive research activity has been organised abroad, at least in the more important industrial countries. During the war we have naturally heard little or nothing of the results gained on the research

Lenning's Institute for Textile Technology, Norrköping.
Knitted goods laboratory.

front. This should, however, not be taken to mean that research activity has been inhibited or stopped. On the contrary, we have every reason to believe that research has been intensified in every respect. Even if it is used in the first place in the services of war, it will be of very great importance also in a more peaceful future. The same was experienced as regards conditions during and after the last war. The unprecedentedly rapid development, not least in the sphere of textiles, may largely be attributed to the research results which were "stored" during hostilities and could only have their effect in times of peaceful international intercourse. In all probability we may await a similar development in quick tempo as soon as conditions have, to some extent, been stabilised after the present confusion. It will be proved more than ever before that carefully organised research activity is an indispensable condition of the power of a country to withstand competition.

At long last, we in Sweden also have the necessary bases to be able to foster textile research on the essential scale.

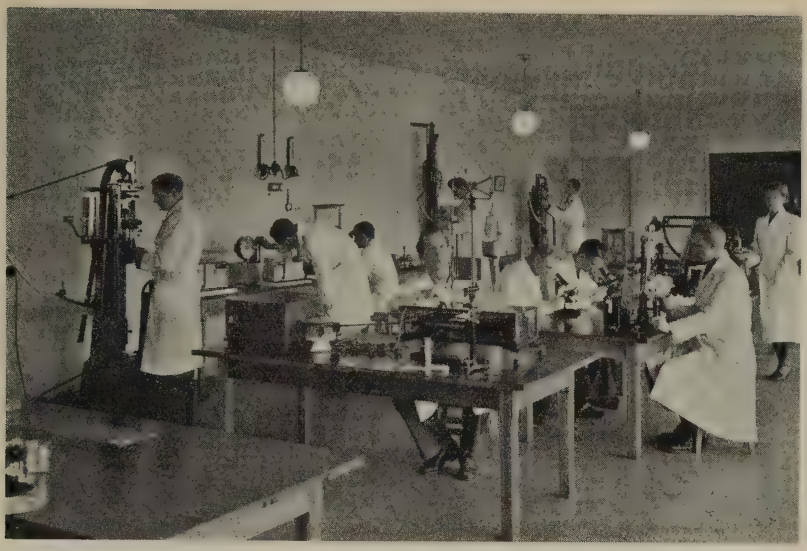
The Textile Institute in Borås. Exterior of projected extension (right wing).

The Textile Research Institute in Gothenburg and the textile institutes in Borås and Norrköping, in addition to the industrial laboratories available for directed research, form together an apparatus of by no means contemptible dimensions. It is now only a question of utilising these resources to the best advantage. It is said that friendship is made to endure longest by gifts and countergifts. If Swedish industry is to reckon with the benefit of foreign research results, our own research must be organised in such a manner that we can give something in return and thus maintain an equal position in this respect. Indeed, it is nothing but in concord with the attitude which Sweden has consistently endeavoured to maintain that we contribute our mite to the common work for international welfare and progress.

The Tasks of Research.

Fortunately our research workers do not lack tasks to perform. The field of basic research, as it has been sketched above, is by no means exhausted. There are still many improvements to be made in the synthetic fibrous materials.

Directed textile research also offers rich possibilities, especially because of its wide range. This applies to the mechan-



The Textile Institute in Borås. The apparatus room of the material testing department.

ical as well as to the chemical problems presented by textiles. As examples of the former we may mention:

The relations between the properties of fibres and those of the final product.

The influence of the various mechanical processes on the quality of the product.

The study of the influence of the cohering power on the mechanical processes.

The rational performance of dressing.

The significance of the evening out of tensions in the thread systems in weaving.

The relation between the manufacturing processes and the shrinkage of textiles.

The effect of thread tension on the density of the mesh in mechanical knitting.

Certain machinery firms have led the way in an exemplary manner with respect to scientifically planned research in textile mechanics, but otherwise the results hitherto obtained may largely be said to have an empirical basis. This field will therefore be a fruitful one for systematic research.

In a similar manner the field of textile chemistry offers a great number of problems in directed research. In this connection one need only consider the work required for the testing in practice of the auxiliary substances, i. e. the preparations named above which are used partly to facilitate the various processes in the manufacture of the fabrics and partly to endow the products with certain improved properties.

Starch chemistry present several unsolved or so far only superficially treated problems. When it is realized what an important rôle the starches and their transformation products play in, for example, the dressing and stiffening of textiles, it should be clear that this subject demands comprehensive research work in order that the processes in question may be fully mastered.

We should also include what may be called "utilisation research" within the concept of applied research. In the clothing industry, it has often been remarked that materials leave much to be desired in relation to their purpose. Undoubtedly a great deal can be done in this territory to achieve better results. Many types of goods continue to exist by virtue of habit; they may have been suited to their purpose in their time, but changed conditions make them no longer rational.

Finally we may include certain border-line subjects within the sphere of directed textile research, in so far as they have application in the textile industry. This especially applies to the study of heat consumption in the various processes of manufacture, whether the heating of a bath or one of the drying procedures is concerned.

In the first case it is a matter of investigating the net heat requirements of the process and of finding how the heat losses could be avoided by suitably designed apparatus. Furthermore the possibilities must be explored of retaining the heat in the baths and avoiding losses at the start and conclusion of the process.

In the case of the drying procedures, a detailed study is required of the power of the air to transport moisture and of the heat transference from the drying surfaces to the material. In drying installations it should also be possible to

Universal yarn-testing apparatus. This measures and registers running variations in the elasticity of the yarn at a certain load.

utilise at least a part of the heat content of the outgoing air for the pre-heating of ingoing drying air etc.

The testing of materials is closely related to research. If it is the task of research to find out the causal connection so that a certain effect may be predetermined, then it is the task of testing to ascertain whether the desired object has been attained. The methods of testing employed should therefore give a reliable verdict; consequently they must progressively be subjected to critical inspection and revision.

Textile testing methods provide an abundance of subjects for Swedish research and one endeavours to devise methods of such precision that they can be accepted as Swedish standards. There are admittedly a number of testing procedures that are in general use and are widely applied by various authorities in the course of inspection after delivery. The majority of these methods, however, may be described as unreliable.

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This brief summary can do nothing more than indicate the extent of the field of textile research. We can establish with satisfaction that we are now beginning to acquire the resources necessary for the cultivation of this field. It is necessary, however, that we also have expert workers devoted to their task.

And perhaps most important of all: we must maintain an increasingly intimate contact between research and industry. Research must not lose contact with practical life. On the other hand industry must realise that research is an essential part of industrial life as a whole. Research and progress are indissoluble concepts.

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Reflections on Scientific Research and Industrial Development.

By Harald Nordenson.

In 1918, The Svedberg published a collection of scientific essays under the title *Research and Industry*,[1] and even at this early date he presented his views on the importance of scientific research for the promotion of industrial development and general material advancement. As motto he cited the following words by Priestley[2]:

"From Natural Philosophy have flowed all those great inventions by means of which mankind in general are able to subsist with more ease, and in greater numbers upon the face of the earth."

He adds in his preface:

"The technical application of scientific results has enabled us to increase enormously our production of goods, in fact all our material civilisation is founded on it. We must clearly realize that research and industry — this word taken in the meaning of production of material goods — are both equally important to us." "We must take care to create favourable conditions for the production of scientific knowledge, which is just now so extremely important to us."

Thus, The Svedberg at a very early stage expressed his ideas on the intimate connection between scientific research and material development.

These ideas of his have later been emphasized on different occasions in his lectures and other statements. About ten years ago, Svedberg took up contact with some industries in

[1] *Forskning och Industri,* Naturvetenskapliga Essayer, Hugo Geber Stockholm 1918.

[2] *History of Electricity* 1767.

order to put his laboratory with its exceptional resources at the disposal of the men of industry for the investigation of problems which they had not the means and qualifications to solve. The writer had the great satisfaction of establishing some of these connections. This collaboration has grown so rapidly that at present the Institute of Physical Chemistry in Uppsala, under the guidance of THE SVEDBERG, occupies a unique position — I believe we may say not only in our country — as a centre of scientific research for the benefit of industry.[1]

In 1938, the Royal Swedish Institute for Engineering Research (*Ingeniörsvetenskapsakademien*, *I. V. A.*), together with the Federation of Swedish Industries (*Sveriges Industriförbund*), appointed a committee for the advancement of technological research. The committee made contact with THE SVEDBERG, and made many of his views its own. The result was a petition to the Government to appoint experts for the investigation of this matter in collaboration with representatives from the institutions mentioned.

In 1940, the then Minister of Commerce appointed a committee to investigate measures to be taken for the promotion of technological research. All were very satisfied to learn that THE SVEDBERG had accepted an invitation to join this committee and taken upon himself the by no means inconsiderable burden involved. Among those who have followed the work of this committee, it is unanimously agreed that the results have in many respects been deeply influenced by the very great interest which SVEDBERG has shown, as contributor both to the debate and to the work on several sub-committees, e. g. those for food products research and textile research.

When the committee, in its first report, proposed the creation of a permanent State Council for the Promotion of Technological Research, SVEDBERG's membership was a matter of course, and to the general satisfaction he followed up his valuable earlier contribution by accepting.

During the work of the committee it was very often pointed out and emphasized in different quarters, especially by

[1] For further particulars the reader is referred to a paper in this book by RAGNAR WINBLADH, page 675.

Svedberg, that besides all the measures proposed by the committee to promote technological research, there always remained an eminently important task: to create better foundations for all these measures by promoting pure scientific research in the sphere of mathematics and pure science.

Ways and means to attain this end were often discussed in committee, as well as privately between members, and the idea was considered of raising the question in the Swedish Parliament (*Riksdag*). At the beginning of this year's session a members' bill was introduced in both chambers of the *Riksdag*, calling attention to the importance of research in mathematics and science and requesting the government to take the matter up.

As this bill is the outcome of deliberations in which Svedberg has taken a very active part, and also contains a summing-up of the present situation, it may be of some interest to give a short account of its content.

Before the present war, scientific research in technical problems was chiefly pursued at our Universities of Technology (*Kungl. Tekniska Högskolan*, Stockholm, and *Chalmers Tekniska Högskola*, Gothenburg), at several institutes connected with the Royal Swedish Institute for Engineering Research (*I. V. A.*) and at some few laboratories run by the larger industrial works. During the war, however, several important steps have been taken.

In 1940, a committee was appointed to promote inventions which might be expected to be of value, especially during the war, for defence purposes or general utility (*Uppfinnarenämnden*). This council has an annual allowance of 200 000 crowns for investigations and experiments.

In the previous year an organisation was initiated by the *I. V. A.* to promote contact and collaboration between all those connected with technological research (*Forskningens Beredskapsorganisation, F. B. O.*). This organisation has on several occasions put the authorities in contact with the proper experts when a special question has suddenly arisen and has also arranged meetings and discussions on subjects of immediate interest.

The above-mentioned Committee for the Promotion of Tech-

nological Research was appointed in August 1940. As an outcome of its work we may mention the following results of its initiative:

An annual allowance to the Universities of Technology of 150 000 crowns for the promotion of research at these schools.

A state council for technological research with an annual allowance of 700 000 crowns.

A committee for building and construction research with an allowance of 200 000 crowns.

A new building for and reorganisation of the Metallographic Institute.

An institute for forest products research.

An institute for textile research.

An institute for geotechnological research.

Other questions under consideration are food products preservation and food products storage etc.

In other spheres also, the need for organised research work has been acknowledged. Committees have been appointed to investigate ways and means to promote medical, sociological, and agricultural research.

So far, however, very little has been done to promote pure scientific research. Owing to the great financial strain caused by armament production, the public grants to the universities have on the contrary been reduced.

The Universities of Uppsala and Lund have had to fall back on their own funds, but they cannot in the long run stand the strain. It is no exaggeration to characterize the present situation of scientific research in our country as critical. A radical change is an imperative necessity.

Pure scientific research is the necessary foundation of all research directed to practical ends. This has been strongly emphasised by the Committee for Technological Research, who maintain that fundamental research work is quite as important as applied research work for the general development. The committee adds: "We are justified in saying that the advancement in the standard of living which has, except for some years of war, progressed continuously, is essentially the result of research work, and a constant following up of this research

work is necessary in order that our country may maintain its position among the nations."

Before the present war it could be asserted with good reason that a small country could only achieve a limited amount of research work. The exchange of results was comparatively free between countries and this was especially the case with regard to science. The growing tendency to autarchy in many countries has greatly diminished the exchange of scientific results, and this makes it necessary for all countries to build up research on a national basis. It has therefore become an absolute necessity to subsidize pure scientific research on a much larger scale.

The close connection between fundamental and applied research work has also been pointed out in other connections. Thus the Minister of Public Education pointed out, when speaking on medical research work, that the progress of medicine has to a very large extent profited by the results of fundamental science (physics, chemistry, physical chemistry etc.).

It is a fundamental characteristic of pure scientific research that it is, generally speaking, unbound. A man of science need not trouble about the direct use that may be made of his results. Obviously research work of this kind will always find it difficult to compete economically with research work directed to certain ends, which has the possibility of giving solid practical results. It would, however, be most short-sighted if we neglected pure scientific research in favour of the more practical research work. The results of scientific research are the sources from which practical research and technology draw their material. If the source runs dry, the activities dependent upon it will dry up.

The necessities for the promotion of scientific research are adequate localities, resources, and sufficient auxiliary forces. In many cases the institutes of our universities and high schools offer quite satisfactory localities, but those who have to run them are greatly handicapped by unsatisfactory resources and lack of assistants. It is absolutely necessary that a radical change take place in the endowment of our university and high school institutes. Money spent on them should be considered as an investment with the possibility of yielding very ample dividends. Necessary means of attracting clever young students

and encouraging them to take up scientific research are to award scholarships at a more advanced stage and to appoint assistants at reasonable salaries. This would simultaneously solve the problem of providing enough qualified collaborators for the directors of the institutes.

The post war competition between nations will no doubt be intensified. The only means for small nations to assert themselves is to aim at the highest possible quality. But quality can only be based on a high technical standard, and this implies highly developed scientific activity. One of the main conditions for maintaining and improving our standard of living, therefore, is that we promote and keep up a highly developed scientific standard.

Scholarships of 2 500 crowns are now available for advanced students at the Universities of Technology and students of law. Such scholarships must be created also for advanced students of mathematics and science. It is also of great importance that the young scientists be offered help in publishing their works, especially their doctoral theses. For this purpose a total sum of 18 000 crowns is now available. The Royal Academy of Sciences also has a sum of 85 000 crowns per annum at its disposal for printing papers in its own proceedings. These sums must be augmented lest the number of papers published by our young scientists decrease.

The bill ends by proposing that the *Riksdag* should request the Government to investigate means to ameliorate conditions of research in mathematics and science and to place before the *Riksdag* such proposals as may seem appropriate.[1]

[1] The bill in question was passed by both chambers of the *Riksdag* on June 21st, 1944. (NOTE ADDED IN PROOF).

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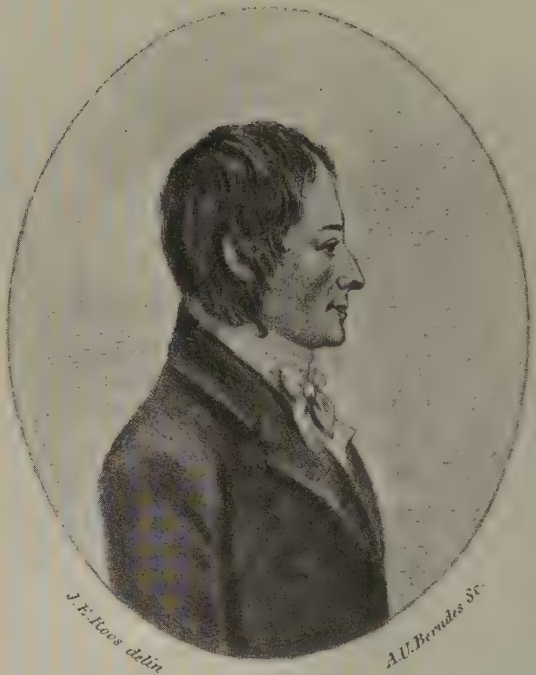


A. G. EKEBERG

Chemiæ Laborat. Ups.
Reg. Acad. Scient. Holm.
et Reg. Soc. Scient. Ups. Membr.

Anders Gustaf Ekebergs kemiska föreläsningar 1805—1811.

Av Arne Westgren.

K. Vetenskapsakademien, Stockholm.

Berzelius meddelar i sina självbiografiska anteckningar, att han under sin studietid i Uppsala saknade möjlighet att åhöra sin mest uppskattade kemilärares föreläsningar. Han skriver: »Ekebergs föreläsningar gåvos privatim och mot särskild betalning. Mina tillgångar ville knappt förslå till nödigt livsuppehälle. Jag måste umbära vad jag icke kunde betala.» Och i konceptet till självbiografien har han tillagt: »Jag beklagar verkligen att aldrig hava hört denne både nitiske och skicklige lärare.»

Om vi sålunda gått miste om en sällsynt omdömesgill lärjunges vittnesbörd om de enda kemiska föreläsningar som vid denna tid höllos i Uppsala — professorn i kemi, Johan Afzelius föreläste mineralogi, f. ö. enligt Berzelius föga njutbart — ha vi ändå en möjlighet att bilda oss någon föreställning om vad akademiadjunkten och laboratorn Ekeberg som föreläsare hade att skänka sina åhörare. Föreläsningsanteckningar av hans hand finnas nämligen bevarade till våra dagar på universitetsbiblioteket i Uppsala. De äro bundna i en volym (D. 1502) med titeln »A. G. Ekeberg. Kemiska föreläsningar m. m. 1805—1811.» Av en anteckningslapp, inhäftad innanför pärmen framgår, att manuskripten år 1859 skänktes till biblioteket av den kände geologen och kemisten Axel Erdmann (1814—1869), skaparen av Sveriges geologiska undersökning. Det första bladet bär följande med blyerts skrivna anteckning: »Hedersbror Erdman, såsom veritabel Kemist, täcktes bevara och hålla dessa blad etc. till godo och i förvar. — Rsm 1842. Utredare av Sterbhusets Papper har jag icke haft hjertelag

att, Vulcano Sacrum. gifva dessa blad. — Den döende Kemisten, Lärarn och Vännen brände nästan alla, innan sin utslockning, af ej fulländade analyser m. m. etc. etc.» Signaturen Rsm har igenkänts tillhöra militärläkaren med. dr. och kirurgie mag. Olof Abraham Robsahm (1784—1849).

Volymen innehåller c:a 300 sidor föreläsningsmanuskript och 40 sidor strödda anteckningar av olika slag, bl. a. reflexioner rörande Bertholletts affinitetslära, kemiska recept och ett utkast till en recension av Berzelius lärobok i kemi. Papperet är av hög kvalitet, och väl bibehållet; skriften, om ock på sina ställen fin och hopträngd, är vårdad och lättläst.

Ekeberg var en klassiskt bildad man. I hans eftermäle i vetenskapsakademiens handlingar för 1813, det år han avled, meddelas, att redan då han som tolvåring 1779 åtnjöt undervisning i Söderåkra prästgård i Småland »väcktes hans håg för den Grekiska Litteraturen, hvilken under hela hans lefnad och ända till slutet utgjorde hans uppmuntrande läsning.» Han hade också en utpräglad litterär ådra. Från hans yngre år finnas bevarade patriotiska oden och tal, begravningsdikter, en saga, »Skördemännerne», skriven på anmodan av landshövding Schröderheim »för att presenteras åt hans Maj:t, den unge konungen, under dess vistande i Upsala vid Jubelfesten år 1793», och en godmodigt gäcksam satir över riksdagens förhandlingar i form av en »Prospectus till en ny Riksdags Tidning». Föreläsningsanteckningarnas klara språkliga form vittnar också om att de äro skrivna av en man med litterär talang.

De uppsatser som Ekeberg publicerat i vetenskapsakademiens handlingar över titanmalmen från Käringbricka, den svarta stenarten från Ytterby (gadolinit) och upptäckten av tantal i den »problematiska zinngraupen» från Kimito i Åbo län visa, att han var en för sin tid ovanligt kunnig och skicklig kemist. I sin artikel »Om chemiska vetenskapens närvarande skick» i Litteraturtidning för år 1795 framträder Ekeberg som banbrytare i vårt land för Lavoisiers idéer och kritiserar dels Scheeles berömda avhandling om luften och elden dels Grens »Systematisches Handbuch der gesamten Chemie» från 1787, ett verk, som att döma av dess citerande i föreläsningarna var en vid de kemiska studierna i Uppsala vid denna tid an-

litad uppslagsbok. Av föreläsningsanteckningarna framgår också, att Ekeberg var en vaken forskare, som påpassligt följde med framstegen inom sin vetenskap.

Föreläsningsmanuskripten äro till antalet fyra och ha, att döma av överskrifterna, författats för vårterminen 1805, höstterminen 1806 samt vårterminerna 1809 och 1811. Anteckningarna för 1805 äro ganska kortfattade, och för 1811 har endast en begynnelse om några få sidor gjorts; de sistnämnda sluta mitt i en mening. Vårterminernas anteckningar, som inbördes förete vissa likheter, ha tydligen legat till grund för elementära kurser. Manuskriptet för 1806 är betydligt mera omfattande och av större intresse än de övriga. Där göres ett försök att rädda Torbern Bergmans affinitetslära från det slag som nyligen riktats mot den genom Bertholletts teori om den kemiska jämvikten.

De elementära föreläsningarna ha avsett att meddela en koncentrerad översikt över vad man på den tiden visste om de olika elementen och deras föreningar. Det därvid använda teckenspråket har ännu åtskilliga drag gemensamma med de alkemistiska och farmaceutiska symboler som göra Scheeles manuskript så svårtillgängliga för vår tid, men i många stycken förebådas redan det av Berzelius sedermera införda mera rationella beteckningssättet. Metallerna symboliseras sålunda med bokstäver men omgivna av cirklar. Natron och kali tecknas med N och K, stundom med S och P, omgivna av trianglar med spetsen nedåt och de alkaliska jordarterna med C, S och B, omgivna av trianglar med spetsen uppåt. Ett ämnes sura karaktär representeras med ett åt höger utdraget horisontellt streck. Saltsyra och flusspatsyra tecknas med M och F, omgivna av kvadrater varifrån utdragits ett kort streck åt höger. Sedan man också lärt sig de stenografiskt korta tecknen för svavel, fosfor, kolsyra och ammoniak, möter det ingen svårighet att följa framställningen. Över huvud taget är beteckningssättet konsekvent och lättöverskådligt; det måste sägas väl motsvara vad som var erforderligt i en tid, då den kemiska stökiometrien ännu var föga utvecklad.

I sina inledningar till dessa föreläsningar har Ekeberg visat sig ha en framsynt uppfattning om kemiens förhållande till angränsande vetenskaper. I anteckningarna för 1805 står att

läsa: »Chemia Physica har ock blivit räknad till använd Chemie; men som den rena Chemien begynner just där som Physiken slutar, så kan Chemia Physica icke innehålla något annat än det som utgör grunderna af den rena Chemien och består af de kunskaper, i hvilka bägge vitenskaperne på sin obestämda gräns sammanguta sig.»

Mycken tankemöda har lagts ned på föreläsningarna under hösten 1806. Inledningen är ett vältalighetsprov, som förtjänar anföras. Ekeberg börjar den 1 oktober sitt föredrag på följande sätt:

»Vi mötas här Mine Herrar för at gemensamt under dessa månader sysselsätta oss med en vetenskap, hvars värde för menskliga förståndets odling icke af någon sanningsälskare kan misskännas, hvars inflytande och medverkan är lika så välgörande vid lifvets behof och mödor som vid culturens finare anspråk på beqvämlighet. Rikedomen och vidden af dess område har sysselsatt forskningsgåfvan i förbigångna århundraden och lämnar oändeliga utsigter till verksamhet för de kommande. De sistförflutna decennierna, en Bergmans och Lavoisiers tidehvarf synas oss likväl utöfver de föregående hafva varit rikt på upptäckter af stora sanningar. Det må vara genom en synvilla, at de fält, som ligga oss närmast visa oss objecterna större och vigtigare, då de aflägsnare förekomma oss mindre betydliga och förlora sig ur sigtet. At kämpa med fördomen och vidskepelsen var kanske för de gamla ett större och mödosammare värk än det nu är för oss at fredligt lyfta slöjan af den ena natursanningen efter den andra, sedan ledtråden ur labyrinthen en gång är gifven. Men skörden intresserar oss och faller mer i ögonen än första brytningen af sterila marken.» Hur skulle studenterna reagera, om en kemiprofessor i våra dagar inledde en föreläsningsserie med en dylik retorisk overtyr?

Det kan kanske synas överraskande, att Ekeberg på tal om de stora kemiska upptäckarna vid 1700-talets slut glömmer att nämna Scheele, men vid denna tid insåg man ännu ej, att Scheele var större som forskare än Bergman. Ekeberg har tydligen också under sina studieår i Uppsala kommit att genomträngas av en bergfast övertygelse om sanningen i Bergmans lära om de kemiska elementens elektiva attraktion. Denna

teori tycktes bringa reda i kunskapen om de kemiska reaktionerna. Bergmans stolta lärobyggnad hade emellertid nu kommit i fara genom Bertholletts arbeten, och Ekeberg insåg, att hans grundsyn på de kemiska omsättningarnas natur var starkt hotad. Han skriver:

»Den Bertholletska Reformationen ligger värkeligen djupare och sträcker sin värkan långt allmännare än den Lavoisierska. Ty ehuru många omständigheter fingo efter Lavoisier en annan förklaring så lämnades likväl stora sträckor av Chemiens område i sitt fordna skick. Men efter Berthollet måste hvarenda fläck på fältet ombrukas, hvarenda fåra få en annan rigtning. Ty det är just själfva attractionsprinciperne, hvarifrån vi utgå, hvilkas laga kraft han drager till forum och det är svårt at tänka sig någon reform av större vigt.»

Liksom de flesta kemister vid denna tid ansåg också Ekeberg de Bertholletska teserna innebära, att de kemiska föreningarna ej skulle ha konstant sammansättning, en konsekvens som han ej var hågad att acceptera. Han utlåter sig härom på följande sätt:

»Efter den Bertholletska theorien är således en kropp likasom liknögd och likgiltig för alla slags proportioner af förening med ett annat ämne, och således blir här alldeles ingen fråga om öfvermättning, emedan efter hans idé alla mättningsgrader äro lika naturliga.»

Emellertid finner han, att åtskilliga av de experimentella iakttagelser på vilka Berthollet bygger äro obestridliga fakta, t. ex. den ofullständiga dekompositionen av kolsyrat kali med kalk, och den nya teorien kan därför ej utan vidare avvisas utan måste upptas till ingående granskning. Liksom andra forskare vid den tiden och även senare finner dock Ekeberg Bertholletts framställning något dunkel. »Berthollet har uti sin tractat Recherches sur les lois de l'affinité», skriver han, »hvarken uppställdt sina satser uti system på ett ställe, ej heller har han på de ställen, hvarest han kommer till deras exposition, och som sker här och där i afhandlingen alt som de sammanhänga med och bevisas af de anförda experimenterne, uttryckt sina idéer med fullkomlig klarhet och precision, utan värkeligen lämnat än det ena obestämdt, än det andra så exprimeradt, at det lätt kan tydas i en annan mening, så-

som jag straxt härefter med exempel skall visa.» Vid beskrivningen av Bertholletts teori håller han sig därför huvudsakligen till dennes tyska uttolkare, G. E. Fischer och F. K. L. Karsten.

Innan han skildrar och kritiserar Bertholletts affinitetslära anser han det emellertid nödvändigt att först ingående precisera vetenskapens förutvarande ståndpunkt på det område som den franske forskaren vill reformera. Han tecknar därför mycket omsorgsfullt och utförligt Torbern Bergmans lära om den kemiska attraktionen. Dessa sidor torde vara de mest läsvärda av dessa föreläsningsanteckningar, ty här ha vi en utläggning av en intelligent adept av läran om den kemiska valfrändskapen, som ger oss 1700-talskemisternas syn på affinitetsproblemet i ovanligt klar form. Hur bokstavligt Ekeberg uppfattade den kemiska attraktionens väsen framgår av följande uppslag till undersökning:

»Det kunde vara värdt, at i anseende till frändskapen mellan alkali och syra göra försök, huru deras utvärtes dragning harmoniserar med den Chemiska. Månne ej en droppe af syra och en af alkali yttra dragningskraft till hvarann på större afstånd än ett par vattendroppar eller ett par droppar af likartad materia. Försöket kunde göras på en med fettma gniden glasskifva.»

Sedan han avslutat sin skildring av Bergmans teori, uttrycker han sin beundran för densamma i följande med blyerts tillskrivna rader:

»Sådan var den affinitetslära, som upprättades af Bergman, ett verk, som utan tvifvel blir i alla tider ansedt för ett stort företag af menskliga snillet både för rikheten af de därvid med otrolig flit samlade fakta, som för den skarpsinniga blick hvarmed de blifvit bedömde.»

Han redogör därefter utförligt för Bertholletts teori, som avhandlas under en följd av föreläsningar. Och slutligen tar han upp den fråga, som tydligen ligger honom så varmt om hjärtat: Kan Bergmans affinitetslära ändå trots allt icke räddas? Han rycker in till dess undsättning, och det sker på det sätt som är vanligt, då vacklande lärobyggnader skola stöttas upp; han söker bygga ut den. Hans sätt att resonera framgår av följande avsnitt ur föreläsningarna:

»Sedan jag nu Mine Herrar med Herrarna genomvandrat och besett den nya och efter påstående fastare byggnad, som Bertholler upförde till ett tryggare residenz för vår vetenskap, och jag bjudit till at lämna ingen omständighet, ingen vinkel obemärkt, där antingen hela localen eller blott inredning och utsigt af det gamla blifvit förändrad, så vill jag nu försöka, at på ett och annat ställe i Systemet kasta en granskande blick och därvid framställa de anmärkningar hvartill jag tycker mig vara befogad. Hvar och en upmärksam practicus måste vara eller, lätt kunna blifva öfvertygad om sanningen af de facta, som Bertholler lägger till grund och rigtigheten af det därpå grundade omdöme at svårigheten at åtskilja chemice förenade ämnen absolute ifrån hvarandra är vida större än man efter attractionstabeller och fordom gällande regler velat föreställa sig, at jag esomoftast vid sådane tillfällen får i stället för ett rent ämne urskildt, ett som qvarhåller en lott ur sin förra egendom eller en ny tillagd, at ehuru mycket svagare jag anser ett ämnes affinitet emot ett annat, så värkar det i sin mon genom densamma hvad det förmår, så länge det står qvar inom attractionssphaeren, och at vid dess afvikande därifrån den äfven rätt ofta utöfvar den rätten at i detsamma värka med sin affinitet och släpa något med sig. Detta alt vore fåfängt at vilja vederlägga. Men med ärkännande af det hufvudsakliga i systemet i synnerhet hvad som rörer det practiska, vilja vi efterse, om icke någon grundsten här och där kan ligga mindre fast, om ej theoretiska synpunkten någon gång förryckes, och om icke det föregående systemet ännu till en del har sina välgrundade påståenden och anspråk, som förtjena att tagas i betracktande.

Om vi skulle vara nog vågsamma metaphysici at återgå till deductionen af de olika hufvudqvaliteter vi känna hos materien, så borde väl alla de särskilda krafter, som agera vid chemiska processer kunna härledas ifrån första constructionen af materia uti attractiv och repulsivkraft. Alla olika tillstånd hos kroppar uti form och förbindelse, skulle då bestå uti modificationen af dessa krafter, uti ett olika förhållande i actionen imellan den utvidgande kraften och den inskränkande. Följacktligen skulle alla hos Bertholler anförda särskilda krafter som han sätter emot affiniteterne, nemligen rigiditet,

elasticitet, värme, efflorescenz, uplösningsmedlets värkan hänföras under samma generella ansickt och altsammans vara särskildta sätt, hvarpå materier inbördes draga och stöta tillbaka hvarandra, och det allmännaste begreppet för allt blef lättheten eller svårigheten för materier at ingå förening med hvarandra, det vill säga olika affinitet. Det vill säga: gamla systemet har icke felat däruti at det satt olika affinitet såsom grundsats, utan däruti at den ej betracktat sin grundsats ur en nog hög synpunkt, at det tagit de i ärfarenheten förekommande phaenomener, såsom en omedelbar värkan af några vissa kroppars affiniteter, då actionen borde betracktas såsom vida mera sammansatt och af en djupare grund. Jag skall straxt för at ej blifva oredig uplysa detta med ett exempel och liksom göra ett språng ur det abstrakta i den kännbara verlden. Låt en löst förening decomponeras af ett tillsatt ämne och den afskilda kroppen utkristallisera därifrån. Låt för at ännu mera försinnliga saken och framställa den för ögonen exempel tagas af Benzoesyrad kalk, som decomponeras af saltsyra, hvarvid Benzoesyran afskiljer sig genom kristallisation. Nu hette det efter electiva affinitetssystemet: Saltsyran hade större affinitet till kalken, därföre måste Benzoesyran vika. Men det heter efter Bertholletts system: Benzoesyran utskilde sig i följe af sin egen kristallisationskraft. Men jag vill anse det för attraction altsammans blott at actionen icke blir så enkel utan mycket komplicerad. Jag måste här betrackta affiniteten emellan Kalken och Benzoesyran, Kalken och Saltsyran, vattnets affinitet till hvardera af dessa ämnen och deras föreningar, attractionen mellan de homogena enkla particlarne i hvart ämne, hvaraf kristallisationskraften ej kan vara annat än en modification. Alla dessa affinitetscollisioner och kanske flere obemärkta determinera nu resultatet.»

Hans fortsatta utveckling av detta ämne är mera metafysik än kemi. Måhända ha omdömesgilla åhörare vid denna del av föreläsningsserien hellre sett tid och kollegieavgift använda för andra ändamål.

De som gått till dessa föreläsningar för att få en inblick i kemiens senaste framsteg måste dock ha känt sig tillfredsställda med den översikt som under terminens senare del meddelades över de nyligen gjorda elektrokemiska upptäckterna

av Davy, Carlisle och Nicholson, Berzelius och Hisinger m. fl. Även de sista föreläsningarna, som ägnats kolets föreningar med syre, väte och svavel, ha förvisso erbjudit åhörarna mycket av intresse. De experimentella landvinningar som därvid skildrats ha lyckligtvis ej inbjudit föreläsaren till några spekulationer över hans favoritobjekt, de kemiska attraktionsprinciperna, som under föreläsningsseriens förra del ständigt lockat honom bort från realiteternas mark.

Vid tiden för Berzelius studier i Uppsala, som inföllo mellan 1796 och 1802, hade Berthollet ännu ej skrivit sin Recherches sur les lois de l'affinité och hans Essai de statique kom ut först 1801. Ekeberg hade vid denna tid knappast någon anledning att så utförligt som skedde 1806 i sina föreläsningar dryfta frågan om den kemiska affinitetens väsen. Att döma av hans vetenskapliga författarskap på 1790-talet hade hans intresse då starkt fångats av Lavoisiers skrifter, och han studerade ingående skotten Lubocks Dissertatio Physico-Chemica, som bygger på de antiflogistiska idéerna. Ekeberg var då en vägrödjare för modern kemisk forskning i Sverige, och det var sålunda säkerligen icke utan skäl som Berzelius vid skildringen av sina ungdomsår beklagar, att han ej hade haft möjlighet att åhöra hans föreläsningar.

Summary.

Anders Gustaf Ekeberg (1767—1813), the discoverer of tantalum, was teacher of chemistry at the University of Upsala. The University Library possesses a series of his lecture notes from the years 1805—1811. They correspond to four different courses of lectures, three of which are of an elementary kind while the fourth, given during the autumn of 1806, seems to be intended for a more advanced audience. The former are of interest mainly from the point of view of chemical notation. Some of the alchemical and pharmaceutical symbols used by Scheele are still utilized but, on the other hand, the more rational notation of Berzelius is foreshadowed. The lecture manuscript of 1806 is by far the most extensive one, dealing with Torbern Bergman's doctrine of elective attraction principles and Berthollet's new theory of

chemical equilibrium, both of which are very minutely reviewed. An attempt is made to save the affinity theory of Bergman from the threats of the new ideas. An extensive and very clear description is also given of the electrochemical researches recently performed by Davy, Carlisle and Nicholson, Berzelius and Hisinger, and others. The lectures end with a report on the new discoveries of carbon monoxide, hydrocarbons, and carbon disulphide.

The manuscript written in 1806 seems to be a document of considerable value to the history of Chemistry, giving a very clear representation of the eighteenth century chemists' conception of chemical affinity.

Manuskriptet inkommet den 21 maj 1944.

A. G. Ekebergs gravsten å Uppsala kyrkogård.

Science and Chemical Industry in Collaboration.

By Ragnar Winbladh.

Associated Chemical Industries (Centralbolaget för Kemiska Industrier A.B.), Stockholm.

When a new product of chemical industry is placed on the market, there lies behind its appearance a long chain of activities in which, in one form or another, the scientific results of fundamental research constitute the first and most important links. Thus without intimate collaboration with science, chemical industry cannot live. Every day the progress continues at ever increasing speed and every day, therefore, this collaboration acquires increasingly vital significance. Chemical industry cannot live, as it once did, on occasional impulses, followed by a pleasant rest on laurels won. To-day the collaboration between the scientific research and chemical industry must be organised solidly and effectively, so that the workers in fundamental research may continuously exchange ideas with the chemical engineers and the leaders of industry. In this manner a constant stream of new life is led into the chemical industry.

As far as Sweden is concerned, the collaboration between science and industry has considerably advanced during the war and has already clearly left its mark upon the development of chemical industry. I hope to be able comprehensively to illustrate this collaboration with the following single example from the viewpoint of chemical industry. This refers to the collaboration between The Svedberg and his institute on one hand, and many of the leading chemical industries of the country on the other. Svedberg is engaged in pioneer fundamental research in those spheres which increasingly enter the foreground of modern chemical-industrial development. This

applies above all to Svedberg's researches concerning large molecules, which increase, stage by stage, the possibility of industry taking these large molecules into its service. Research in this sphere demands such laboratory organisation and equipment that even the best financed industrial laboratories cannot find the resources necessary for more detailed high-molecular research. For industry, therefore, it has been of inestimable value that The Svedberg has not isolated himself in his research institute, but has cooperated with the Swedish chemical industry, thus providing for the direct participation of the rich knowledge and powerful resources of the Institute in industrial development.

In respect of organisation this collaboration has been gradually developed, and its present character may be described as follows. Contact is first made between the directors of the chemical concern and Svedberg concerning the fundamental lines of collaboration. With the aid of chemists from both quarters a working programme is drawn up, but not so rigidly, however, that it cannot easily be adapted to the experimental results as they are obtained. For the commencement of the working programme, suitable personnel is obtained either from within the Institute or by fresh appointments. The work is planned so far in advance and under such economic conditions that qualified research workers may be engaged. These workers begin their task by visiting the chemical plants for which they will work, where they thoroughly acquaint themselves with the technical processes and problems which concern their investigation. The industry also appoints chemists to follow the work in Uppsala by visits and correspondance. Thanks to this personal reciprocation the research work becomes a living thing, adapted to the desires and aims of the industry. Personal contact with the Institute in Uppsala is also illustrated by the fact that at seminars, discussions of doctor theses, and lectures, representatives of chemical industry are quite often to be seen among the audiences. In the lecture theatre of Svedberg's institute one frequently observes industrial leaders who have voluntarily "returned to school" to listen to scientific lectures and discussions. The doors of both

the Institute and the SVEDBERG home stand hospitably open to visiting industrialists, and in the guest-book of the Institute the names of many Swedish and foreign celebrities are to be found.

In certain cases collaboration has been organised in an even more intimate manner. In one case, for example, three industrial enterprises in Stockholm[1] have built, with SVEDBERG as "background" a joint research laboratory[2] which, with regard to equipment, is modelled where possible, on the Institute for Physical Chemistry in Uppsala. One of SVEDBERG's closest collaborators has been appointed head of the laboratory, the work of which is planned by him in consultation with SVEDBERG and an industrial representative. It may thus be said that the Institute has opened a "branch" in Stockholm.

To take charge of the manufacture of SVEDBERG's mechanical apparatus, which have been developed for several decades in the well-equipped and skilfully directed workshop of the Institute, a company[3] has been established parallel with the joint research laboratory mentioned above, which, in its precision instrument workshop, will manufacture apparatus designed by SVEDBERG and his collaborators for Swedish and foreign research institutes as well as industrial laboratories. Examples of these are the oil turbine ultracentrifuge, the equilibrium centrifuge, the surface balance, the stream double refraction apparatus and LAMM's diffusion apparatus. In this connection it is of interest to note that the company in question has also entered into similar collaboration with Professors SIEGBAHN and TISELIUS with respect to apparatus designed by them, such as the SIEGBAHN molecular pumps and the TISELIUS adsorption analysis and electrophoresis apparatus. It should be added that the company will also manufacture fine chemicals, especially those which are a result of work in the joint research laboratory. All this activity is designed

[1] *Liljeholmens Stearinfabriks A.B., A.B. Kema* and *A.B. Stockholms Bryggerier.*

[2] *Forskningslaboratoriet LKB.*

[3] *LKB-Produkter Fabriksaktiebolag.*

to give assistance to research in its own interest and in that of industry.

An example of the understanding for industry and its methods which THE SVEDBERG and his collaborators have, is provided by the fact that the Institute is organised according to purely industrial principles. The research workers are freed from all routine work. At the ultracentrifuges, for example, samples are sent in by the different workers. These are dealt with by well-trained operators who then pass on the results to the so-called calculation department, where the operations are divided into different sections, exactly as in a well-organised workshop engaged in mass production.

Several of the contributions to this book provide concrete examples of the collaboration between THE SVEDBERG's institute and industry. It may be added, in quite general terms, that despite the fact that our chemical industry is based especially upon the forest as its raw material, the relevant fundamental research problems have been considered so wide and complicated at the Institute that only in recent years have they been attacked. Now, however, that the start has been made, very great resources have been drawn upon in order to deal with the fundamental problems of wood chemistry. The desire, arising from both technical and economic considerations, to press on ever further with the refining of cellulose, has necessitated a study of the structure of its large molecules and the changes which these undergo in the technical processes for cellulose treatment. These investigations are supported in the first place, fittingly enough, by a great cellulose enterprise. In their auxiliary developments, however, they are of interest to the explosive industry, which has for several years employed Swedish refined cellulose instead of imported cotton in the production of nitrocellulose, and to the artificial silk industry. The nitrocellulose investigations also extend into the sphere of the lacquer and plastics industries.

The high-molecular technical product which at all times during the present war has been a centre of public interest is synthetic rubber. So much has been written and spoken about what THE SVEDBERG and his collaborators have done

in this matter that I shall only say, in all brevity, that because of the fact that technical information available was not sufficient, it was necessary in the neoprene synthesis to start from the beginning. The Institute therefore had to attack synthetic problems in pure organic chemistry and, in later stages, purely mechanical questions concerning construction of apparatus and machinery. It must be considered remarkable that recently, only some years after the commencement of the research, it has been possible to start a factory for the large scale production of neoprene. There is no doubt that in several respects the American methods available have been improved upon, simplified, or abandoned altogether and replaced by new processes. This is especially the case where the Institute's particular sphere is concerned, namely the conversion of simpler molecules to large molecules, i. e. polymerisation procedures. During the rubber research in Uppsala, both on a small and a large scale, a large number of chemists and engineers have received a training from which the Swedish organic-chemical industry will derive great benefit in the future.

There is no institution in the country which has such a mastery of the chemistry of artificial resins and plastics as the Institute for Physical Chemistry in Uppsala, and most chemical enterprises which are concerned with these matters are in direct or indirect contact with The Svedberg. The development abroad in this sphere is probably the most revolutionary that has occurred in these materials. Artificial resins are beginning to appear everywhere both in technology and in the household. I need only name as examples articles of bakelite, carbamide and melamine plastics, nylon silk, plexiglass, artificial resins for electrotechnology and the cable industry, artificial resins for divers adhesive purposes etc. If we are to hold our own in the industrial development in this branch, our success will greatly depend upon the degree to which science and technology collaborate.

Proteins long constituted the Institute's most cherished sphere of high-molecular research and here collaboration took place with both medical men and biologists. Industry, however, has also shown great interest in these investigations.

This applies especially to the brewing industry, on behalf of which the role of proteins in the brewing process was studied. Work was started with the grain, proceeded by way of the intermediate products, and ended in a study of the proteins in the final beer and an attempt to establish their influence on the quality of the product.

Our fat-chemical industry has also begun to realise the importance of high-molecular research. In this territory many scientific successes, including methods for the analysis of fat mixtures, have been achieved in Uppsala, and will probably prove to be of industrial importance.

It might be thought that industry, with the great burden of work which it lays on the shoulders of The Svedberg and his collaborators, would cause the research spirit to deteriorate. In reality the opposite is the case; the impulses that reach the Institute in the course of its collaboration with chemical industry also have an encouraging and catalytic effect on fundamental research activity. There are many examples of cases where industry has confronted The Svedberg with a problem of detail, which, in the course of solving, has been so generalised by Svedberg, that in the end a solution has been reached to a problem of wider significance. It is also a fact that the material resources placed by industry at the disposal of the Institute have been greatly to the benefit of higher science. All parties have thus derived pleasure and advantage from the fruitful collaboration between The Svedberg and the Swedish chemical industry.

An expression of the general appreciation for The Svedberg's work to the benefit of chemical industry is evidenced by the fact that in May this year the title of Doctor of Technology *honoris causa* was conferred upon him.

Manuscript received May 26th, 1944.

Från Nya Kemikums första tid.

Av J. Arvid Hedvall.

Kære *The*. När du nu fogar ihop dina tiotal till en hexagon, så veta vi alla, som känna både dina och den kemiska sexhörningens egenskaper, att ringslutningen icke betyder ett fullbordat lopp. Den sexlediga kärnan innebär inom kemins värld intet tillstånd av *parum affinis* utan fastmera ett stabilt komplex med rika möjligheter till påbyggnad och utväxt. Där god samverkan mellan inre och yttre betingelser finnes, råda enahanda förhållanden i människans liv. När skulle sådana utsikter te sig gynnsammare än i den forsknings miljö, du skapat omkring dig. Under ditt sjätte decennium har du med nya banbrytande undersökningar byggt upp en ny solid bas för ditt arbetes stormolekyl, vars mångsidiga, för forskningen i lika hög grad som för tillämpningen betydelsefulla utvecklingsmöjligheter icke ligga inom det sannolikas område utan inom det säkras.

Men det hör till mänsklig egenart att från en uppnådd utsiktsplatå ej endast blicka ut över nya vidder. Perspektivet över den tillryggalagda vägen med dess växling mellan branta stigar och plana nivåer har sin speciella tjusning. Vi, som voro med dig under dina första forskarår, tro, att du med särskild glädje skall fästa din blick på den delen av färdvägen, de kemikumår, som föllo inom ditt eget tredje decennium. Vi tro det icke endast därför, att de åren voro för dig och oss alla i fackligt hänseende inriktande och bestämmande, utan även, emedan den tidens redan klassisk vordna kemistmiljö med dess förebildliga samspel mellan arbete och kamratlighet säkerligen också gav oss för livsföringen omistliga värden även av annat slag.

Det är sant och ofrånkomligt, att varje människa ser vävnaden av personer och händelser på sitt eget sätt, och att

både verkligheten och dess minnesbilder få den förnimmandes egen bearbetning, även den måhända växlande och påverkad av andra intryck. Men då vi, som bildade denna krets, träffats efteråt — det må ha skett ofta eller sällan, ett par av oss eller många — så har det undantagslöst visat sig att vår lärotid och våra första forskarår på Kemikum hos oss alla kvarlämnat det gemensamma intrycket av en idealisk samvaro, där arbetet och spörjandet aldrig hämmades men väl främjades av ett kamratskap, som växte till ett vänskapsband, vars fasthet gott tålde de påkänningar livet alltid bjuder, och som höll oss samman, trots att kretsen under åren spreds över stora avstånd. Oupplösligt binder oss det bandet också vid minnet av dem, som under de år, som gått, lämnat oss, Yngve Björnståhl, Gustaf Hellsing, Otto Holmberg, Fredrik Jahn, Ivar Nordlund, Sven Odén, Ludvig Rinman, Håkan Sandqvist och Ragnar Widman voro alltför särpräglade gestalter och skänkte oss var och en på sitt sätt för mycket för att någonsin glömmas.

I slutat av 1800-talet vällde på nytt en våg fram av ökat intresse för kemi och fysik, mäktigare än någon tidigare. Dess verkningar spårades redan i gymnasiernas föreningsliv, och vid de redan gamla universitetsinstitutionerna uppkom en olidlig trängsel. Där fysik och kemi bo under samma tak, blir kemisten i längden så obekväm för fysikern, att den senare inte har något emot att bli av med den osande, apparatfarlige grannen. Så blir det i regel kemin, som först av de två blir herre i eget hus. Gamla Kemikum i Upsala hade också länge illa svarat mot tidens krav, både kvantitativt och kvalitativt. År 1904 stod en ny byggnad färdig att tagas i bruk, och på sommaren det året skedde överflyttningen till de nya lokalerna. Den ägde rum under P. T. Cleves ledning med hjälp av vaktmästarna och Upsalas berömda, till allt användbara stadsbud. Cleve knogade själv på vågar och andra ömtåligare apparater. Dåvarande kandidaten Artur Bygdén och licentiaten Otto Holmberg lämnade också uppskattad hjälp, särskilt vad biblioteket beträffar.

Cleve avgick med pension på våren 1905 efter att under föregående hösten ha varit tjänstledig. Det var hans hopp

Amanuenser av olika årgångar på Nya Kemikums trappa 1913. Stående fr. v. A. Westgren, G. K. Almström, N. von Zweigbergk, T. Svedberg, E. J-son Virgin, R. Widman. Sittande fr. v. H. Sandqvist, O. Holmberg, J. A. Hedvall (med Almströms hund Tommy), N. Pihlblad. Foto: I. Nordlund.

att efter inträdd pensionsålder helt få ägna sig åt sin stora passion under senare år, diatomacéerna. På försommaren 1905 gav han sig ut med ett sjömätningsfartyg på Västerhavet för att samla plankton men förkylde sig och dog i juni samma år.

Widman förestod under Gamla Kemikums sista år det analytiska laboratoriet, där docenten Daniel Strömholm och fil. dr. E. L. Rinman voro amanuenser. Strömholm arbetade med jämviktsundersökningar i system av basiska metallsalter och Rinman med triazolföreningar. På organiska avdelningen regerade med mycket sträng hand licentiaten Alfred Ekblom, som sedermera disputerade (1903 i Lund) på en avhandling om derivat av ortoaminobenzolsulfonsyra.

Det dröjde ej länge, innan den nya institutionens rymliga salar för övningslaborationer fylldes av den snabbt växande skaran av tillströmmande unga kemister och medicinare. Syntessalen kunde taga emot cirka ett femtiotal, och inom kort blev

det nödvändigt att anordna dubbla kurser per år. Specialaboranternas antal växte också snabbt, säkert fortare, än vad som hade beräknats, ty även på Nya Kemikum funnos relativt knappt tilltagna utrymmen för forskning. Snart upplåts därför generöst plats för licentiatlaboranter på de båda professorslaboratorierna. Amanuensernas expeditionsrum erbjödo knappast några arbetsmöjligheter av denna art. Dylikt fick utföras i respektive övningssalar, där dessa tjänstemän fingo eget bord och dragskåp. Undersökningarna voro både i oorganisk och organisk kemi ännu så lagda, att en mera invecklad eller ömtålig apparatur icke behövdes vid det dagliga arbetet. Någon större olägenhet av detta system förmärktes därför knappast. Man kunde till och med tala om vissa fördelar genom den bättre kontakten mellan lärare, amanuenser och lärjungar av olika slag. Ett faktum är, att vi på denna tid togo så livlig del i varandras arbeten, att vi kände andras uppgifter och resultat nästan lika väl som våra egna. Något hemlighetsmakeri fanns sannerligen inte under någon period av våra kemiska läroår.

Det fordrades ingen utpräglad clairvoyance för att förutsäga, att The Svedbergs inträde i Upsalas kemiska miljö skulle bli av största betydelse. Då Cleve vårterminen 1904 höll sin sista föreläsningsserie över de sällsynta grundämnenas kemi, satt på främsta bänken i salen en vetgirig ung man, om vilken en annan åhörare av dessa föreläsningar vittnar, att man ej gärna kunde undgå att lägga märke till honom. Det var The Svedberg, som inskrevs som student vid universitetet i januari 1904. Sedan han efter egen utsago övervunnit en viss tvekan inför valet mellan kemi och botanik och bestämt sig för kemin, gjorde han redan från allra första början av sina rekordmässigt få akademiska läroår upp en arbetsplan, vars originalitet och klara sikt mot målet skulle förvånat, även om det gällt en i forskningens vildmark och snår länge tränad vetenskapsman och inte en tjugoåring. Svedbergs val av kemins arbetsfält berodde på att han insåg, att denna vetenskap erbjöd större möjligheter än botaniken till intim materieforskning. Det var det då ännu i fundamentala avseenden obearbetade problemet om materiens molekylstruktur som lockade och via kolloidkemin målmedvetet angreps enligt nya metoder. Det länder

den tidens universitetsmyndigheter till heder, att inga hinder restes i hans väg. Men det är också karakteristiskt för föremålet för denna festskrift, att han aldrig begärde mer än det absolut nödvändiga, och att hans arbets- och kostnadsplaneringar redan från början präglades av klarhet och saklighet. Det säger sig emellertid självt, att dessa starkt fysikaliskt betonade experimentarbeten krävde andra lokaliteter och annan utrustning än vad övriga på institutionen bedrivna undersökningar fordrade.

Svedberg förordnades som nybliven fil. kand. efter 1 ¾ års universitetsvistelse till amanuens, och sedan övningsarbetena avslutats installerade han sig i de rum i norra flygelns entresolvåning, som under lång tid framåt skulle utgöra hans förvisso ganska anspråkslösa laboratorielokaler. Ljudet av sjungande motorer och sprakande induktorier och anslag med varning för ledningar med livsfarlig spänning tillhöra mina första (ht. 06) intryck från den tidens Kemikum. De talade sitt tydliga språk, att i detta hörn av byggnaden höll en ny kemi på att växa fram. Det var så självklart för alla, att vanliga tidsberäkningar och svårhetsgrader förlorade sin betydelse, när det gällde Svedberg. På ett naturligt och opretentiöst sätt gick han förbi alla andra. Endast Ekbom var litet irriterad under den »organiska kursen». Han tyckte, det gick för fort. Men eftersom allt var riktigt, var det ju inte mycket att göra. Vaktmästare Lönn berättar emellertid, att Ekbom kom en kväll efter stängningsdags och sade: »det går alldeles för fort för Svedberg, jag skall nog ge honom svårare uppgifter och se vad han duger till.» »Men» — jag citerar fortfarande Lönn — »han gjorde även detta så, att Ekbom inte kunde hitta någon anmärkning.»

Det fanns i den nya kemiinstitutionen en förmån för amanuenserna, som utom dess reella värde också kom att betyda synnerligen mycket för hela den anda, som blev något erkänt karakteristiskt för arbetet och samvaron på Kemikum, nämligen de utmärkta bostäderna. Tre dubletter och ett stort enkelrum (egentligen 1 ½ och därför någon gång benämnt »Sesquium») beredde trevna hem åt fyra amanuenser. Det var den södra delens nedre och övre entresoler, som bildade denna kavaljersflygel. Dessutom fanns en dubblett i det lilla trähuset,

Amanuens T. Svedberg vid sina apparater. Foto: I. Nordlund.

det s. k. Lilla Kemikum. Den femte amanuensen, som skötte de organiska övningslaboranterna, kallades av någon anledning »biträde vid övningarna». Det ansågs litet finare, och befattningen var också bättre betald. Då Harald Nordenson vid en middag, given av det nyvordna »biträdet» G. Karl Almström, höll tal till värden och lyckönskade honom att ha introducerats i *akademimonden*, föddes för en gångs skull en vits, som är värd att ihågkommas. Men det var en händelse, som låg flera år framåt i tiden.

Widman utnämndes 1905 till professor i kemi och blev den nya institutionens förste prefekt. Fyra år senare blev Strömholm ordinarie efter att en tid ha fungerat som laborator och e. o. professor. Uppdelningen dem emellan, vad deras kemiska domäner beträffar, var från början given, och så kom den organiska kemin under Widmans ledning att förläggas till övervåningen och den oorganiska under Strömholms till den nedre etagen. Den fysikaliska kemin fick sin egen lärostol först genom den personliga professur, Svedberg 1912 erhöll. Emellertid hade Carl Benedicks 1904 utnämnts till docent i fysikalisk kemi, och han föreläste bland annat över elektrokemi och sitt speciella intresse, metallernas fysikaliska kemi, inom vilket senare område han ända till sin avflyttning som professor i fysik vid Stockholms Högskola 1911 bedrev undersökningar på institutionen tillsammans med O. Tenow. Hos Benedicks arbetade dessutom Ragnar Arpi med metallografiska problem. Han medföljde till Stockholm för att sedan ägna sig åt tekniskt forskningsarbete i Uddeholmsbolagets tjänst. Åren 1904 och 1906 hade docenternas krets ökats med Ludvig Rinman och Otto Holmberg. Den förre började tidigt syssla med det, som skulle bli hans livsgärning, teknisk organisk kemi, och lämnade under våren 1906 sin amanuensbefattning. Han kom först till Skutskär i Bergslagets tjänst och arbetade bland annat med att utvinna produkter ur svartlut. Detta förde honom vidare till utexperimenterande av en natroncellulosametod. Sina senaste år tillbringade han utrikes och dog 1938.

I Holmbergs under flera år fortsatta arbeten med sällsynta jordarter levde Cleves anda kvar. Under sina amanuensår (1904—1909) sysslade han oavbrutet med sina omkristallisationer för isolering av jordarter. Hans doktorsavhandling (1906)

bär titeln »Om framställning af ren neodymoxid och om tvänne nya metoder för separering af sällsynta jordarter». Senare arbetade han med renframställning och atomviktsbestämning av holmium.

Vi, som började på »syntesen» ht. 1906, fingo våra prov rättade av Holmberg eller av Svedberg, som redan året förut avancerat till amanuens. Han efterträdde Gustaf Hellsing. Denne, gemenligen kallad »Gutten», disputerade 1905 över »α-aminonitriler och α-aminotiamider» och slog sedan i likhet med Rinman in på den för en akademiker i de åren ännu ovanliga banan som teknisk kemist. Hellsing sysslade först med oljeutvinning ur skiffer och sedan med försök att framställa uranradiumpreparat ur kolm. Under de senare åren av sitt liv — han dog 1928 — ägnade han sig i Nerike åt skifferdestillationsproblem.

På dörren till de båda rummen i södra flygelns övre entresol stod The Svedberg, Fil. Kand., om det visitkortet nu verkligen hann bli färdigt, innan Fil. Lic. fick komma istället. I dubbletten ifråga erinrade länge tapeterna — en, om jag minns rätt, i ljusgrått med ett diskret mönster i rosa — om The, som var denna bostads förste innehavare och själv målat dem.

Sannolikt var det redan under denna tid, som ett brev med adressen

To
the Svedberg
Upsala
Sweden

anlände. Avsändaren anade väl knappast, hur signifikativt detta »the» med litet t var.

Varken Hellsing eller Bodman, som också var amanuens, bodde i institutionsbyggnaden utan ute i staden. Rinman däremot torde ha varit den förste gästen i den amanuensdubblett i första entresolen, där Håkan Sandqvist sedan under många år hade sin bostad, möblerad med vackra gamla saker från borgmästarehemmet i Hudiksvall.

I min dagbok för den 6 oktober 1906 finner jag följande: »Var på Kemikum hela dagen. Demonstrerade för Svedberg.» En senfödd *civis academicus* bör häri icke inlägga någon modern

T. Svedberg i sitt amanuensrum. Foto: I. Nordlund.

betydelse i ordet demonstrera. Handlingen innebar ingen som helst opinionsyttring. Demonstration betydde en uppvisning av framställda preparat av en viss metallgrupps föreningar. Hade man något så när handlag med dessa laborationer, så voro de rätt snart överstökade. Jag anlitar fortfarande dagboken och finner, att kursen började den 2 oktober, och att Svedberg godkände Viking Dunér och mig den 13. Ur den välkända gråspräckliga boken är nedanstående anteckning

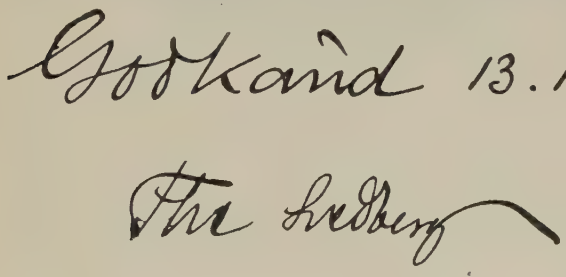


Foto: I. Nordlund.

tagen. Dunér och jag, i egenskap av de först utsläppta, utsågos att ordna med ett allmänt synteskafferep ett par dagar efteråt. Räkningen, som jag har i behåll lyder

Carl G. Gester, Konditor
Drottninggatan 3

Okt. 15. An 45 kaffe med bröd à 0,30 13:50

Bröd och kaffe voro allt annat än knappt tilltagna.

Vaktmästare P. J. Larsson vid »djurens utfodring». De senare äro fr. h. K. G. Tham, S. Odén, J. A. Hedvall. Foto: I. Nordlund.

Säkerligen är det Karl Ivar Nordlund, redan under skoltiden med någon utbyggnad av de två förnamnsinitialerna benämnd Kivet, som från denna synteskurs (ht. 06) tagit den bild, som visar vaktmästare P. J. Larsson stående i förrådet vid den förrättning, som brukade kallas »djurens utfodring».

Det nämnda kafferepet blev det första i en lång rad av dylika synnerligen gemytliga tillställningar på det trivsamma, men därför icke mindre arbetsfyllda Kemikum. Från professorernas sida rönte våra små fester full förståelse, till och med

då det hände, att det knastrade och small vid välkända hastiga steg i ett par smärtingskor. Det var på golvet utlagt knallkväve, som i all oskyldighet exploderade.

Den 1 november (1906) började »kvalis» med blåsrörsanalys som första etapp. Amanuenser voro Otto Holmberg och Ragnar Widman, som var speciallaborant för Strömholm och sysslade med en fortsättning av dennes arbeten över föreningar mellan kvicksilver och ammoniak, arbeten, vilkas resultat år 1912 framlades i gradualavhandlingen: »Studier över ammoniakaliska kvicksilverföreningar.» »Ragnar Junior» bodde naturligtvis i fadershuset i Gamla Kemikum. Han blev rektor i Nyköping och så småningom undervisningsråd. Han dog 1932. Ett par karakteristiska porträtt av denna tids amanuenser från »kvalis» — de liksom de flesta här förekommande från »atelier Kivet» — bifogas här. Otto Holmberg kom 1911 till Kontrollstyrelsen och dog som laborator där 1934.

Minnena från »kvalis» äro väl för många förenade med de amanuenser, som kommo efter de nu nämnda, nämligen Nils von Zweigbergk (1907—1914), Erik Virgin (1909 och 1914) och Erik Söderbäck (1912—1930). Den förstnämnde — med intimnamnet Adelsmannen, eller så småningom kort och gott Adel — bodde först i en länga i Geijersgården och senare som oförglömligt gemytlig granne (1913—1914) i dubbletten högst upp på södra sidan, där han efterträdde Erik Virgin, som i sin tur kom dit efter The Svedberg.

Adelsmannens distraktion var liksom hans kamratliga hjärta av översvinnliga mått. Hundratals laboranter skola vid återkallandet av hans bild se honom i det lilla amanuensrummet letande bland högar av papper och tobaksburkar efter den alltid bortkomna nyckelknippan och höra honom med låneord från Infernos rike efterlysa den till vanställdhet inrökta pipan, med vilken han var oupplösligt förenad. Då han till sist behövde bägge händerna för att leta och munnen för att högljuddare ropa ut sin längtan, återfanns vanligen pipan — antingen i den ena handen eller i — munnen. Särskilt »laborantskorna» skola också minnas honom, då han smått generad å deras vägnar med tröstande ord lämnade åter en analys med »± 2» eller kanske rent av med ett »orätt». Djupt etsat i erinringen står också Adels olycksöde med sitt efter en lång

O. Holmberg vid sina jordartsarbeten. Foto: I. Nordlund.

prövande tid äntligen läkta ben, då han på nytt vid en halka i Slottsgränd bröt upp såret. Troget satt han ändå strax efteråt på sin plats på amanuensrummet med alla de upptornade old-english-burkarna bakom sig och med en fylld bläckpenna spänd till en katapult och riktad mot dörren. Den inträdande fann en sorgsen Adel och hälsades med: »Bror får akta sig, jag vill skvätta bläck på vem fan som helst.» Nästan ännu mera prövande för Adelsmannens kynne blev provåret 1914. Hans depression, icke minst genom tanken på att lämna Uppsala, rörde oss så djupt, att han på Håkans förslag under denna period befriades från att »blanda och ge» under våra pokeraftnar.

Under åren på kursen i kvalitativ analys fick von Zweigbergk en imponerande erfarenhet om analytiska ting, och många metodiska förbättringar härröra från honom. Om dylika frågor handlade också hans avhandlingar.

Amanuens N. von Zweigbergk (t. v.) och R. Widman (t. h.). Foto: I. Nordlund.

För Erik Virgin, som licentierade för Widman, blev allting ett minutiöst precisionsarbete, det må nu ha varit hans undersökningar av explosiva derivat av oxalyldiacetofenon, publicerade 1914 i gradualavhandlingen »En ny typ av diisonitrosoperoxider», eller av mera profana ting. Vi kunna lätt framkalla hans bild och se honom putsande sina kameralinser, elegant suveränt behärskande den av honom introducerade mikroelementaranalysen eller med samma hängivelse beredande en raktvål med dittills ouppnådda egenskaper. Denna operation, som han en tid med förkärlek ägnade sig åt på expeditionsrummet, föranledde Håkan att införa beteckningen »raktvåleri» på sådant, som han tyckte var bortkastande av tid.

Erik Söderbäck började redan på övningskurserna arbetena med framställningen av fri rodan. Den idén hade han redan från skoltiden, och hans undersökningar, framlagda i dissertationen »Studien über das freie Rhodan» (1918), ledde också

till önskat resultat. Vi, som voro hans kurskamrater, minnas, hur han redan under övningslaborationerna stack emellan med egna experiment och hans entusiasm över någon lyckad reaktion, som han visade oss. Söderbäcks rodanexperiment hörde under senare stadier inte alltid till de mest välluktande. Syftande härpå står under rubriken *Utnämningar* i *Chemisches Skandalblatt* följande: »Till prefekt på stinkavdelningen har utnämnts förre nattvakten därstädes fil. lic. E. Süderbach». Både ordet »nattvakt» och följande alfabetvers:

»Söderbäck går ut på svaj
mårtensgås och första maj»

häntydde på hans betydligt regelbundnare livsföring än de andra amanuenskavaljerernas. Det blev både sång och spel framför hans dubblettdörr, då vi kom hem från en fest, från vilken han smitit, enligt vår mening för tidigt, ty hans försynta väsen gjorde honom till en högt skattad kemikumkamrat. Hans renvins-mecenatskap vid de så kallade natriumfesterna får väl i det sammanhanget ej heller glömmas.

När man klarat de torra, våta och sammansatta proven och slutproven och tenterat för Strömholm inne i hans s. k. »lejonkula», som fick sitt namn genom kombinationen med Daniel och sannerligen inte genom någon omild behandling därstädes — den var tvärtom den hänsynsfullast tänkbara — så dröjde det vanligen en tid, innan man kunde börja på »kvantis». Denna övningssal, då belägen i nedervåningens norra fasadhalva och hörn, var nämligen väsentligt mindre än de andra. På »kvantis» fungerade vt. 1907 Gösta Bodman som amanuens. Under våren 1906 tycks Svedberg ha beklätt denna befattning och att döma av följande, hämtat ur *Svensk kemisk Nidskrift* för våren 1906, synes han då och då ha förfärat laboranterna med en smula livligt förlöpande reaktioner. Versen är tagen ur ett allmänt kväde till amanuensernas respektabla krets och börjar:

Amanuenser, rysansvärda ord.
Ja, ärade herr' kavaljerer,
det tänker faktiskt var och en som ser er,
att rysligare släkt finns knappast på vår jord,

T. Svedberg (t. v.) som amanuens på »kvantis» och W. Nisser (t. h.).
Foto: I. Nordlund.

samt fortsätter efter harangering av Gösta, Otto och Håkan med:

Se'n The, vi från kritik ej heller kunna dig befria,
fast du är ung ännu och barnsligt snäll.
Ty våra analyser du förstör, var gång du med en ryslig smäll
uti en eldstod höljer dig som Sankt Elia.

I den gestalten finna vi honom på följande bild.

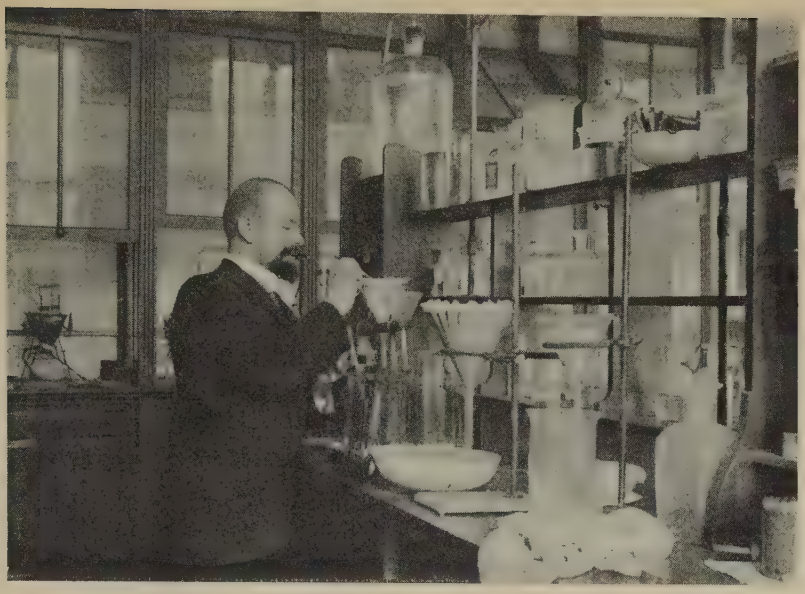
En av kvantislaboranterna under Svedbergs amunuenstid där var Per Geijer, som har i livligt minne den händelse, som bragte The i den på nästa bild återgivna 'modifikationen'. The höll på med att slå ihop gamla koagulerade eterlösningar av kolloider i en kolv med ett stort natriumnystan i. Etern började plötsligt koka, varför han höll kolven över slasken. Plötsligt kom en 'krevad' åtföljd av en intensivt gul låga, som slog rätt upp i ansiktet på The. Redan nästa dag satt han emellertid, ehuru till oigenkännlighet ombunden, på sin trebening och omdestillerade eter igen.

Bodman skötte sin amanuensbefattning liksom alla andra under sitt liv med den schwung och det goda humör, som

»Eyeless, noseless and lipless, bandaged from brow to chin.»
Foto: P. Geijer.

säkerligen var en stor tillgång under den i många avseenden påfrestande sydpolsexpeditionen, i vilken han deltog 1901—1904. Bodman tog efter hemkomsten ånyo itu med kemin. I Antarctis blev det väl mest meteorologi, och att döma av den mörklagda och starkt uppsvällda kortleken även diverse priffe och wira eller vad det nu kan vara, som man på den tiden spelade vid Sydpolen. Hans disputation ägde rum 1906 på avhandlingen »Isomorfi mellan salter av vismut och av de sällsynta jordmetallerna».

På »kvantis» ägde ett slags separering rum mellan dem som gjorde »stora kvantis» och tänkte fortsätta och licentiera eller åtminstone taga högsta betyget i fil. kand. och dem som nöjde sig med mindre och gjorde den lilla kursen. Men »sägringen» influerade inte på sammanhållningen, som under denna tid tvärtom blev ännu starkare. Kvantislaboranterna intogo också



G. Bodman som amanuens på »kvantis».

ett slags mellanställning mellan de vetenskapsidkande och kurserna. Man fick en vink om, att det var lämpligt bli medlem av *Kemiska Sektionen*, och det kunde till och med hända, att man erhöll förtroendet att utföra analyser åt någon forskande äldre broder. Om inte förr så hedrades man nu av de äldre och amanuenserna med titelbortläggning. Denna procedur, som väl än idag kan äga rum under så enkla former som vid ett tillfälle jag minns: »goddag bror, jag känner visst inte dej förut», underlättades ytterligare genom det likörbryggande, som av ålder ägde rum någon gång under denna kurs. Den eterdenaturerade alkoholen bragte inte brygden i klass med certosabrödernas. Snarare kanske med nuvarande rakvattenblandares. Det blev faktiskt glest i lederna en gång under Ångströms fysikföreläsning, vars eleganta experiment och förkunnelse hade förtjänat ett uppmärksammare auditorium än de få halvsovande naturvetare, som trots allt lyckats komma i tid. Det var nog närmast dylika kokkonster, som åsyftades, då följande stod att läsa i nyss citerade *Nidskrift* av år 1906: »Fil. stud. N. Sundstedt Upl. anhåller hos Kungl. Maj:t att få utbyta den stadgade sockerbestämningen på kvantis mot kaffekokning.»

Kafferast på »kvantis» 1906. Fr. v. I. Nordlund, B. Dalén, M. Kolmodin, N. Pihlblad, E. Bengtsson, E. Schön, G. Mikaelsson, E. Bergstrand, E. G. Envall. Foto: I. Nordlund.

Men sådan »kaffekokning» var nu verkligen ett undantag och följderna en olyckshändelse. Vår dagliga sällskapsdryck var kaffe utan eteravec. Det fanns redan vid denna tid en och annan studentska på Kemikum, som sörjde för förplägnaden. På min kvantistid (1907) var det Vivi Högbom, som tämligen regelbundet utfodrade oss med kolvkokt kaffe och wienerbröd från Gesters eller, om det skulle vara fint, med Günthers berömda bisquits, av medicinarna av okänd anledning gemenligen kallade smådjävlar. Fint var det onekligen också ibland, så fint att förnämligare kafferep väl aldrig ha hållits. Som till exempel vid stora tratt-tävlingsfesten, en ädel och praktisk idrott för kemister, som kunde sätta bort mycken tid på för långsamt rinnande filtrertrattar. Det var också den enda sport, som kemisterna ägnade sig åt, d. v. s. med ett lysande *fackligt* undantag, ridningen och ett ej mindre lysande *personligt:* G. Karl Almström körde nämligen bil och flög — ja endast kollyflög förstås — då Chevillard benådade Upsala med dess första passagerarflygning.

Men nu höll tratt-tävlingen på att komma bort bland alla

Fr. v. G. K. Almström och M. Chevillard omedelbart före starten på Polacksbacken 1914. Foto: I. Nordlund.

minnen som droppa fram. Var och en hade valt ut sin bästa tratt, och för en given tid uppmättes sedan, hur mycket som runnit igenom för de olika tävlande. Trattarna hade namn. Jag erinrar mig den vilt rinnande »Niagara», den snabba »Sleipner» och »Daniel i Lejonkulan». En hade ställt upp två till tävling. De hette »Castor» och »Pollux». Efteråt utdelades priserna under en fest, där professorn och damerna serverades kaffe och likör i platinakärl. »Stora och Lilla Mogul» — de två jätteplatinaskålarna — hade fyllts med läckert bakverk. »Syntesens» alla damer, Andrea Andreen, Astrid Devold, Sofia Hugosson, Ingeborg Jungner, Dagmar Wendel och Lilly Westergren (även medicinare gjorde nämligen »syntesen») voro inbjudna på kort och mottogos med sång under ledning av Sven Bohman enligt följande repertoar: 1) »Älvsborgsvisan», 2) »John Browns body», 3) »Scenes that are brightest» ur operan Maritana och 4) »Es war einmal ein Negerkind, das liebte seinen Gott». Någon annan dekoration än denna förtjusande damsextett tillsammans med vår egen Vivi Högbom hade egentligen inte behövts, men vi hade ändå till deras ära

På »kvantis» 1907. Fr. v. V. Dunér, S. Rosén, B. Dalén, S. A. Boman m. fl. Foto: I. Nordlund.

och vår glädje prytt laboratoriet med allehanda symboliska målningar, därav några av Svedbergs hand, och med egenhändigt fabricerade lerbeläten. Otto tyckte emellertid, att det var högst blasfemiskt, då vi föreslog att få tillverka dem av sällsynta jordarter.

Nu skulle man med fog kunna misstänka, att en person, som kom till Uppsala 1904 som fil. stud. och blev docent 1907, inte kunde ha någon tid över för kamratliga nöjen. The tillhörde emellertid ej de s. k. vetenskapliga martyrerna, som älskade att ge sig sken av arbetstyngd och världsviktig brådska. Sådan var aldrig föremålet för denna minnesskrift. Hans sinne för humor och hans konstnärliga och litterära intressen gjorde honom alltid eftersökt även i den kemiska »nöjesdetaljen». Då arbetet tillät, deltog han också gärna lika naturligt road av egna och andras påhitt som vi övriga.

Det är särskilt två episoder, som stannat i minnet från de första kemikumåren: det egyptiska kvantisspexet 1907 och den årligen återkommande repliken av »Otto retas i Sachsiska Schweiz». Vår »kvantiska» Uarda kom visserligen av någon

anledning aldrig till uppförande, men det gjorde egentligen mindre. Vid detta, liksom vid de flesta andra evenemang av denna sort, är det som bekant förberedelserna, som spela den största rollen. The's livliga fantasi och konstnärliga anlag blommade vid målandet av kulisser och andra dekorationer. Tyvärr har det ej lyckats mig få tag i några rester av dessa alster, där kemi och egyptologi ingått i den sköna förening, som i detta fall har antikt klassisk bakgrund. Medregissörer till The voro Sven Anselm Bohman och Seth Rosén, en »dubblett» som betydde mycket i »kvantis'» konstnärliga tillvaro.

På sommaren 1908 hade The, Håkan, Ragnar och Otto företagit en studieresa till Tyskland för att titta på diverse industrier. Otto lär ha varit »Führer», och den fras, han svarvat ihop vid ankomsten till ett nytt ställe: »Wir wollen die Fabrik besichtigen», kan sägas vara i stil med vad som nu för tiden inlägges i detta begrepp. Att konstruktionen hade närmare sammanhang med kunskaper i tyska, som ej tillåto nämnvärda nyanseringar, än med Ottos själsart, behöver ej påpekas. Nu blir man som bekant emellanåt trött under en resa, och då kan humöret ta slut även i den bästa vänkrets. Av någon anledning råkade Otto ut för denna lilla malör, då sällskapet kommit till Sachsiska Schweiz. På ett för sin naturskönhet berömt ställe hade kvartetten ifråga hamnat, och även det i dessa nejder förekommande 25-pfennigsvattenfallet skulle beses. För att ge ytterligare relief åt dess 25-örighet bemäktigade sig The Ottos paraply och ställde sig rätt under. Ottos ordflöde kunde visst framgångsrikt tävla med vattenditot, och kvartetten lär övergående ha sprängts. Det var denna händelse, som repeterades med Otto vid balkongräcket i entresolen, generad och arg i proportionerna 50 : 50 och med The nedanför, anfallande med en borste på långt skaft. Ibland hände det också, att en kraxande fågel kom in i föreläsningssalen, då Otto hade sin propedeutiska kurs. Jag undrar, om vår jubilar minns, vem som släppte in den!

Otto Holmberg hade fortfarande »syntesen» och avgick som amanuens 1909 för att tillträda platsen som föreståndare för medicinkurserna på Gamla Kemikum. Bodman efterträddes på »kvantis» av Ragnar Widman, och denne åter avlöstes av den tidigare här nämnde Erik Virgin (1909—1913). Efter

D. Strömholm i sitt vågrum 1912. Foto: I Nordlund.

Virgin kom författaren under åren 1913—15 efter att först ha tjänstgjort en termin på »syntesen». Näste man i successionen, både vad syssla och bostad beträffar, blev Henrik Jörlander. Han licentierade för Widman och disputerade 1916 på en avhandling om anisoylfenyloxidoetan.

Oskar Olsson (Collenberg), som under en kort tid (läsåret 1914—15) också var amanuens, och författaren hade för våra licentiatarbeten beretts plats inne på Strömholms laboratorium vilket betydde, att den senare själv generöst avstod hälften av sitt utrymme. Collenberg placerade sina undersökningar inom Strömholms speciella intresse för komplexföreningar och vann resultat, som gåvo ny belysning åt volframs och molybdens lägre valensstadiers kemi. Han disputerade 1914 på en avhandling betitlad »Beiträge zur Chemie des Wolframs und Molybdäns».

Vad mig beträffar, så hade en gammal vid studiet av kri-

stallers modifikationsväxlingar väckt tanke på möjligheten av pulverreaktioner fått nytt liv under torranalysen i samband med uppkomsten av de gröna, blå och röda substanser som vid »blåsning på kol» efter provets begjutning med »koboltsolution» visa närvaron av zink, aluminium och magnesium. Dessa arbetens resultat sammanfattades i doktorsavhandlingen (1915) »Über Reaktionsprodukte von Kobaltoxyden mit anderen Metalloxyden bei hohen Temperaturen». Kemiskt inriktad redan under skoltiden hade jag under mina första läroår närt en svag förhoppning att komma in i kemiamanuensernas frejdade krets. Då erbjudandet kom, uppstod trots detta en viss tvekan. Man bodde inte i enahanda egenskap på det gamla intima Meteorologikum i tre år utan att få starkt fäste där Förnuftet segrade emellertid naturligtvis, och nyåret 1913 möblerades det stora rummet högst upp inåt gården (det redan nämnda »Sesquium»), som tidigare under en kort tid hyst först Pihlblad och sedan en lärjunge till Svedberg, japanen Katsuji Inoye. Då jag efter min disputation (1915) bröt upp från denna bostad och beredde mig att byta ut Upsala mot Göttingen, hade jag nog närmast känslan av att livet var slut. Kemikumrötterna hade trängt mycket djupt. Man kunde ju inte på förhand veta, att den tidens Göttingen och Tammanns Bürgerstrasse 50 skulle erbjuda en miljö, där man snart fick nytt fäste för både arbetet och vänskapen. Snoilskys djupt och sant kända dikt blev mig först senare bekant:

Här i detta hulda hörn av världen
mätt av färden
vandrarn stannar, barmen vidgas fri.
Milt förgätna
på en bänk, där lindens skuggor tätna,
tankens bördor, liksom ränselns, bli.

Utan fruktan att hans byggnad ramlar
drömmen samlar
luftigt virke till en framtidshamn:
där finns Eros
finns musik och blommor och Homeros,
ro och glömska och en öppen famn.

T. Svedberg som nypromoverad i Gästis trädgård $^{31}/_{5}$ 1908. Foto: N. Pihlblad.

De orden passa — vi veta det nu — på mer än en stad, där Alma Mater tagit sin boning. Den tidens miljö, då mitt under ett världskrig mot den lilla universitetsstadens vallar »dämpat svallar fejdens, flärdens sömnlöst yra brus», skall väl också vid något tillfälle få sina minnesblad.

Den 7 december 1907 disputerade Svedberg på sin i Vetenskapssocietetens Skriftserie tryckta avhandling »Studien zur Lehre von den kolloiden Lösungen». Alla kemister voro naturligtvis närvarande och hörde på. Resultatet blev, som tidigare nämnts, en docentur, och det låg i luften, att universitetet beredde sig att ordna så, att det ej skulle gå miste om den unge, redan internationellt bekante forskaren.

Sedan »kvantis» var undanstökad, följde vanligen den s. k. experimentkursen, närmast avsedd att lära blivande pedagoger att utföra instruktiva illustrationer till undervisningen. Dessa övningar ställdes 1909 under Svedbergs ledning med biträde

Från N. Pihlblads disputationsmiddag på Gästis »Ångbåt». Fr. v. K. Molin, H. Andersson, H. Sandqvist, O. Widman, N. Pihlblad, D. Strömholm, E. Söderbäck, J. A. Hedvall, H. Strandberg, H. Jörlander (nästan skymd), E. Söderberg, A. Ångström, T. Svedberg, H. Nordenson, O. Collenberg, A. Bygdén, N. von Zweigbergk. Foto: Ateljé Finn.

av Nils Pihlblad under dennes senare amanuensår. Till 1909 kvarstod Svedberg som amanuens och flyttade sedan till Lilla Kemikum. Pihlblad blev 1909 amanuens och stannade som sådan till 1918. Först tjänstgjorde han på »kvalis» men ännu tidigare (1907) som extra amanuens åt Svedberg vid rening av diverse preparat för hans kolloidsynteser. Det var väl på dylikt handräckningsbehov vid framställningen av allehanda kolloidsoler — givetvis även alkosoler — som följande annons i »*Nidskriften*» alluderade: »Tre kolvdiskare kunna erhålla plats. F. d. brandsoldater ha företräde. Sökanden måste vara nykterist. Lön: olycksfallsförsäkring. The Svedberg». Under åren 1912—1918 bebodde Pihlblad, Otto Holmbergs dubblett högst upp i sydöstra hörnet. Han licentierade för Svedberg och disputerade 1918 på en avhandling med titeln »Lichtabsorption und Teilchengrösse in dispersen Systemen». Vid hans doktorsmiddag på Gästis »Ångbåt» träffades de flesta av de då redan till stor del spridda medlemmarna av den gamla miljön.

Experimentkursen följdes efter en tentamen på Widmans »organiska katekes» av övningar i organisk syntes och analys i övervåningens stora sal och smårum, och där ägde den närmare kontakten rum med den redan då sägenomspunne Håkan Sandqvist, en av de originellaste personligheterna i den tidens student- och studieliv. De som fingo bli hans intima vänner, lärde i honom så småningom känna en man, som med mindre vanlig beläsenhet förenade ett sällsynt gott hjärta och en absolut sveklös själ. Men till att börja med kände man nog närmast en avsevärd fruktan, knappast mindre än den, som hängde i luften från salig Ekboms dagar. Det var den stora skillnaden, att det var en kamratlig respekt. Håkan hade av födsel, borgmästerlig uppfostran och erfarenheter från fenantrensyntesens vanskligheter lärt precisionens betydelse. »Håll dej till ordalydelsen» var hans valspråk, och det tillämpades minutiöst. Bad man få låna en tändsticka, överräcktes denna utan låda och på villkor, att den återlämnades. »Håkofanen» tog den, som beslogs med orena preparat. Kok- och smältpunkter kontrollerades noga. Konstaterades fusk eller slarv, blev det straffsynteser av indol eller skatol, om vilka föreningar man från Widmans bok utom formeln endast lärt, att den ena »luktar vidrigt» och den andra »ännu vidrigare». Gärna utdelades också syntesen av malakitgrönt, som vid oförsiktigt laborerande färgade laboranten grant grön för en tid framåt. Beryktade voro också Håkans skriftliga meddelanden till någon syndare. Alla minnas vi den stackars S-t, som första gången fick lappen: »Kom in, herr S-t, jag vill tala med herr S-t.» När resultatet ej heller vid nästa prov utföll till belåtenhet, kom en ny lapp. »Gör om det, men jag vill inte se honom mer.» Håkan var ingen vän av för mycket fotograferande. Vykortsskrivande hade i honom heller ingen beundrare. Karakteristisk är hans påskrift vid ett sådant tillfälle, då vi andra tyckte, att »ett vy» kunde vara befogat: »God dag, Pihlblad. Hur mår du? Jag mår bra. Adjö, Pihlblad. Sqt.»

Håkan Sandqvist var först amanuens (från 1906) och sedan under många år (1908—13) »biträde vid övningarna i organisk syntes». I denna egenskap hade han sin arbetsplats omedelbart till vänster om ingången till organiska salen, och så var

Biträdande läraren H. Sandqvist (t. v.) och C. Sjöstedt 1913. Foto: I. Nordlund.

även fallet med hans efterträdare G. Karl Almström. Håkans gradualavhandling (1912) bar titeln »Studien über die Phenanthrensulfosäuren», och även i fortsättningen ägnade han mycket arbete åt detta område. Under sin docenttid kom han via bromfenantrensulfonsyror, »den snorformiga substansen», in på de flytande kristallernas problem. Sedermera, framför allt under den tid han uppehöll professuren efter den 1917 pensionerade Widman, sysselsatte han sig med hartskemi, ett område, som han ägnade sitt intresse även under tiden som lektor vid Tekniska Gymnasiet i Härnösand. Han fortsatte därmed även som professor vid Farmaceutiska Institutet, en befattning, som han innehade till sin död 1930. När Håkan sökte professuren och bilade sina många publikationer, bar nr. 1 titeln »Min mineralsamling». Den hade under skoltiden publicerats i tidningen »Kamraten». Ordning skulle det vara.

Under sin första amanuenstid bodde Håkan på Gamla Kemikum och sedermera i den tidigare omnämnda nedre entresoldubbletten, varifrån han avflyttade, då han fick docentstipendium. Håkan var och förblir ännu i minnet en av centralfigurerna i vårt kemikumliv. Hans roll i vårt samliv skulle vara väsentligt ofullständigare, om ej den av honom instiftade »amanuenssupningen» omnämndes. Supning har eller hade åtminstone en bättre klang i Upsala än ordets vanliga. Varje lördagsförmiddag erinrade Håkan om det blivande aftonsamkvämet i det ryktbara *Rum C 11* på Gästis, där under de sista åren den förnämt bedårande Dagmar bringade oss våra enkla drycker. Till denna krets hade även juristen Edward Söderberg fått tillträde. Genom kameratliga förtjänster hade han av Håkan utnämnts till kemist och hedersamanuens. Ofta avslutades vår sammankomst, då krogen stängts, med ett nachspiel i Kanikens (domkyrkosysslomannen Nils Johan Söderbergs) underbara hem i Domtrapphuset, där Edwards något taxliknande hund, Malla, troget väntade i trappan, såvida hon nu inte var med. Men än oftare slöt aftonen uppe hos Nippe; namnet enligt Håkan »efter vetenskapliga grunder härlett» ur det riktiga Nils Pihlblad, vilket aldrig begagnades. I hans kemikumdubblett spelades med ett tämligen konstant lag poker. Drycken var lageröl, som i tur och ordning av amanuenserna beställdes från Bayerska Bryggeriet och förvarades i en kagge på vinden. En gång — jag tror, det var efter Westgrens licentiatfest — hade Nippe smitit hem för tidigt. Hämnden kom. Håkan öppnade hans dörr med en pennkniv, och under betäckning av ett paraply sprutades med en medhavd sifon värden vaken och halades upp till en pokerrond.

P. J. Larsson (död 1935) matade laboranterna ur förråden i nedre våningen och motade ut dem kl. 3 på onsdag och lördag och de andra dagarna kl. 6, då han kom in och slog på sin skyffel. Hans kollega en trappa upp var den lika bestämde men kanske ännu fryntligare A. V. Lönn. Alla från den tidens Kemikum veta, att Larsson och Lönn spelade en roll, som inte beskrives endast av ordet vaktmästare. Vad deras intima kännedom om allt och alla på institutionen betydde för professorer, amanuenser och laboranter av olika slag, kan ej överskattas, särskilt som allt deras görande var präglat av en

Pokerafton i N. Pihlblads amanuensrum 1916. Fr. v. H. Sandqvist, I. Nordlund, H. Jörlander, N. Pihlblad. Foto: I. Nordlund.

aldrig svikande medfödd taktkänsla och kärlek till ungdom och arbete. De voro institutionens tjänstemän på sitt sätt liksom vi på vårt, och de voro och förblevo genom livet våra vänner.

Vid sammanfogandet av dessa minnesblad har jag skrivit många brev och fått lika många svar från den spridda kemikumkretsen. Ett av dem är från vaktmästare Lönn, och det ger liksom alla de andra belägg för vad den tiden var för oss alla. Ett citat ur hans brev må vara nog men också berättigat: »Mina tankar gå tillbaka till den förflutna tiden på Kemikum. Det var många roliga stunder den gamla goda, roliga tiden. Själv var jag ung och fick arbeta bland ungdomen, alltid trevlig. Tiden har gått allt för fort.»

Följande bild visar Lönn och tre av Widmans speciallaboranter, nämligen från vänster Henrik Jörlander, Sven Bodforss och Erik Wahlberg, även kallad »postsektionisten», eftersom han vid Kemiska Sektionens sammanträden i allmänhet först kom till supén. Under föredraget var han kvar på laboratoriet, där vid de tillfällena ingen kontrollerade utfösningen. Längst till höger synes Lönns jovialiska gestalt. Arbetsplatsen var Wahl-

Från »organiska syntesen». Fr. v. H. Jörlander, S. Bodforss, E. Wahlberg, V. Lönn, Foto: I. Nordlund.

bergs hörn av organiska salen. Bodforss var amanuens i två och ett halvt år från 1915, först på »kvalis» tillsammans med Söderbäck och sedan en kort tid på »kvantis». Han bodde på Lilla Kemikum — han tyckte det var för mycket nattsöl och poker i kavaljersflygeln. Fast i allmänhet var han förstås med ändå i Nippes »pokerdubblett». Oskar Olsson-Collenberg, som efterträdde von Zweigbergk på »kvalis» under ett läsår (1914—15), var Bodforss' närmaste föregångare där. Collenberg avflyttade sedan som föreståndare för medicinarnas kemikurser till Gamla Kemikum, i vilken egenskap han efterträdde Otto Holmberg. Bodforss disputerade 1917 på avhandlingen »Till kännedom om aromatiska oxidföreningar» och Wahlberg tre år tidigare på ett doktorsspecimen, betitlat »Om pivalylättikester».

Tidigare men delvis samtidigt arbetade här också Nils Zenzén och Artur Bygdén. Zenzén sysslade en tid omkring 1909 med en av Widman förelagd uppgift att framställa myricylalkohol ur carnaubavax. Han övergick emellertid snart till geologin, där ett stort antal avhandlingar av både mineralogisk, geologisk och geologisk-historisk art av honom publicerats.

Det sista intyg om fullbordade laborationer, som Cleve utfärdade, var åt Artur Bygdén (den 31 maj 1904). Bygdén licentierade i geologi men hade under övningarna på »organiska» (1904) fattat intresse för en av Ekbom åt Matts Essén utlämnad uppgift att syntetisera o-kiselsyreetylester. Som övningslaboration var detta naturligtvis olämpligt, och resultatet kunde ej bliva så fett. Bygdén tog emellertid itu med saken på nytt 1908, vidgade ut ämnet och disputerade 1916 på avhandlingen »Silicium als Vertreter des Kohlenstoffs organischer Verbindungen». Under tiden hade han tillträtt sin befattning som kemist vid Lantbrukskemiska avdelningen på Experimentalfältet, där arbetet fullbordades.

Håkans efterträdare på »organiska» blev som nämnt G. Karl Almström (1913), som tidigare haft både laborationer, från Gillet uppskickade luncher och sin ägandes hund Tommy förlagda till Widmans privatlaboratorium. G. Karl fördelade sitt liv mellan Kemikum, Gillet och bostaden, den s. k. »Vita Hästen»; jag har tvekat något om den ordningsföljd, i vilken ställena böra nämnas. Kanske proportionerna lämpligast beteckna med *ana partes*. Det räcker ju ändå till de säkerligen åtta kemikumtimmarna.

Vi andra åto på någon av »Ambrosiorna», den »store Per Victors» skapelser, på Hushållsskolan eller hos den förträffliga Fröken Sofi på »Åttan», Nedre Slottsgatan 10. Hon serverade där, totalt oförändrad, våra söner ännu för ett par år sedan, då lokalen stängdes, emedan innehavarens av kupongstadgar rörda hjärta utfodrade ynglingarna med den föda, de så väl behövde. På Gillet vittnade emellertid matnamn som *tournedos à la Almström* om att där åt G. Karl, och att hans övade gom borgade för att kötträtten inte i stället borde heta »biff à la Faen», en ändring i beteckning, som Håkan en gång föreslog på en annan krogs något sega föda. Riktigt förankrad blev G. Karl på Gillet efter ett benbrott under en ridning på sin vanliga vita ridhushäst, då han naturligtvis hade svårt att förflytta sig. Det var den sejouren, som slutade med den lysande så kallade »benbrottsfesten», den förut nämnda tillställningen, då Nordenson introducerade beteckningen »akademimonden». Det var också efter den festen, som Almströms bostad Jernbrogatan 1 fick namnet »Vita Hästen», med den sällsport

En afton på »Vita Hästen» 1914. Fr. v. H. Nordenson, H. Sandqvist, J. A. Hedvall, G. K. Almström. Foto: I. Nordlund.

gästfrie värdens — och de tydligen lika sällsynt tungsovande grannarnas — medgivande upplåten till kemikumkavaljerernas ordinarie eftersläckningslokal. Vidstående av Ivar Nordlund arrangerade, halvt allegoriska bild är tagen under en sådan sammankomst.

Det är mer än begripligt, att den stackars värden under sådana förhållanden kunde bli något sen om morgnarna. Olyckan ville, att det också hände en gång, när han var fakultetsopponent. Vi sutto där och väntade och väntade att disputationen skulle börja. Sedan både enkel och dubbel kvart förlupit och ingen akademisk försening längre var tänkbar, skickade Widman slutligen i väg Lönn att väcka och hämta Almström, som, leende som vanligt, skötte sin opposition förträffligt trots fastande mage. I *Chemisches Skandalblatt* förevigades denna händelse några år efteråt: »*Fakultetsopponenter ohoj!* Aktiebolaget Svensk Nattvakt åtager sig väckningar alla tider på dygnet. Säkert och billigt. Referenser: Doc. G. Karl Almström.»

Efter vad författaren tyckt sig förnimma, skulle det befinnas underligt, om ej den till historien gångna händelsen av den 31 mars 1914, »skottet på Vita Hästen», åtminstone omnämn-

des. En afton anordnades där målskjutning. Då författaren till dessa hågkomster skulle skjuta, ansåg sig värden på grund av min ovana vid skjutvapen böra sköta laddningen. Det gjorde han så, att skottet gick mig i benet. Kivet fann ingen anledning att avbryta en påbörjad längre historia, som Fredrik Enqvist förstrött åhörde, men G. Karl och Tommy voro förtvivlade. Åkerlunds brudvagn beställdes, och vi foro upp till Akademiska Sjukhuset men remitterades, då uttagandet av kulan ansågs kunna anstå till dagen därpå. »Mördaren» envisades att erbjuda sin charmanta säng, varför »offret» kvarstannade där över natten. G. Karl låg alltså på golvet, sonande sitt brott. På morgonen ringde en ung dam till min amanuensbostad. Nippe, som bodde bredvid, svarade: »Arvid, nä han är inte hemma, han blev skjuten i går på Vita Hästen och ligger kvar hos Almström.» Till den av den senare anordnade »operationsfrukosten» infann sig snart bemälda dam, diskret klädd i svart och vitt för alla eventualiteter. Det tog någon tid att få henne att lägga om anletsdragen och delta i frukosten. Sedan ställdes på nytt, nu med henne i bröllopskarossen, färden till Akademiska, där Långpelle snabbt tog ut den ytligt belägna kulan.

År 1912 hade Svedberg fått sin personliga professur efter att tidigare (1909—12) med särskilda anslag ha meddelat undervisning i fysikalisk kemi. Den första februari 1913 installerades han med övlig akademisk pompa. Långt tidigare hade lärjungar börjat att strömma till. Det var en hel del upptäckter ute i världen, som i de dagarna varslade om att materiens inre inte var så hopplöst patentlåst, som man tidigare trott. Röntgenstrålar och radioaktivitet kommo med även på kemisternas nyckelknippor, och här hemma bröt Svedberg via kolloidkemin motspänstiga insegel till molekylernas värld.

Sven Odén blev väl Svedbergs förste lärjunge. Hans licentiat- och doktorsspecimen (disputation 1913) gällde det kolloidala svavlet. Experimentarbetet var väl i huvudsak förlagt till det så kallade »sektionsrummet» ovanpå föreläsningssalen. I samband med dessa undersökningar, ägnade han koagulationsprocesser och de faktorer, som därpå inverka, en ingående behandling och kom till resultat av grundläggande betydelse. Senare kom Odén in på sedimentationsanalys och konstruerade

bland annat en automatisk våg för dylika bestämningar. Vi minnas hans arbeten nere i ett av Kemikums icke oväsentliga källarutrymmen. Redan under tiden som docent började han i viss utsträckning den humuskemi, som så småningom gjorde honom speciellt meriterad för den befattning, han vid sin död (1934) innehade som professor vid Experimentalfältet. Tidigare hade han varit professor vid Tekniska Högskolan i Stockholm (1920—25). Ett stort antal avhandlingar, bärande hans även i andra avseenden utpräglade originalitet, vidsyn och skaparkraft, har säkrat honom en framstående plats i vår forsknings historia. Under ett flertal år (1914—19) var Sven Odén amanuens på Kemikum. Han ledde då kursen i föreläsningsexperiment och disponerade, dock utan att bo där, dubbletten efter von Zweigbergk. Under denna tid fylldes på nytt, liksom under den förste innehavarens, Svedbergs, tid, väggarna med böcker av även skönlitterär art. Odén var redan som student ägare av ett synnerligen vackert och välinbundet bibliotek, och hans litterära intressen förde honom tidigt tillsammans med författare. Albert Engström var en av hans och Thes vänner. I vår kamratkrets verkade han kanske mindre hemma. Viljan fattades förvisso icke, och på någon disputationsgask kunde han nog en och annan gång slå sig lös, eller det kanske är riktigare att säga, att han försökte. Men det föreföll alltid, som om det var honom svårt att finna den naturliga uppsluppna tonen. Inom våra led behövs det icke erinras om att vi saknade honom, då han ej var med.

Harald Nordenson, Arne Westgren, Ivar Nordlund och Nils Pihlblad hörde också till Svedbergs första lärjungars skara. Det var onekligen knappt med utrymmet. Lärofaderns eget var icke rikligt tillmätt, och för de övriga fanns väl just intet annat än lokalen bakom föreläsningssalen, ett par rum högst upp i norra flygeln och ett stort och ett litet bredvid biblioteket, ovanpå »kvantis» således, där Benedicks tidigare hade arbetat. Nordenson höll till i ett av dessa senare rum och studerade framför allt kolloidsuspensioners ljusberoende. Han disputerade 1914 på avhandlingen »Über die Bedeutung des Lichtes für die Bildung und Stabilität kolloider Lösungen». Nordenson hade från början åtminstone en del av sin framtidsbana utstakad nämligen som chef för Liljeholmens Stearinfabrik.

Redan under upsalatiden märktes hans organisatoriska och representativa egenskaper, som då på flerfaldigt sätt togos i anspråk inom studentvärlden, och som senare på olika områden, ej minst rörande utformandet av bättre villkor för svensk teknisk forskning, utnyttjats. I kemikumkretsen var hans eleganta och kvicka slagfärdighet en uppskattad tillgång.

Det är med tanke på den senare utvecklingen av Svedbergs arbeten fram till ultracentrifugmetodiken och dess på samma gång djupa och vida betydelse för molekylforskningen och därmed för materiekunskap överhuvud taget långt utanför den rena kemins gränser intressant att följa den första delen av utvecklingslinjen och se, hur de olika arbetena gruppera sig och växa ut. Vi på Kemikum fingo kontakt med dem, redan då han för att använda hans egen beteckning — ett slags inverterad metafor — utdelade sina första »pek». Några titlar torde ge en tillräcklig antydan. Att gå närmare in på innehållet omöjliggör utrymmet och är väl icke heller för läsarna av denna hyllningsskrift nödvändigt. Alltså endast några rubriker från tidigare år: »Ueber die elektrische Darstellung einiger neuen kolloïdalen Metalle», Svedbergs första avhandling (1905); »Über die Eigenbewegung der Teilchen in kolloidalen Lösungen; Ueber die Existens und Eigenschaften disperser Systeme im Grenzgebiet zwischen den kolloiden und kristalloiden Lösungen; Eine neue Methode zur Prüfung der Gültigkeit des Boyle-Gay-Lussacschen Gesetzes für kolloide Lösungen; Über den Nachweis der dynamischen Natur des chemischen Gleichgewichts; Die Existenz der Moleküle; Über die Gestalt der Moleküle; Prüfung der Gültigkeit der van der Waals'schen Zustandsgleichung für kolloide Lösungen; Über spontane Konzentrationsschwankungen in Lösungen und Gasen; Über das elektrische Leitvermögen anisotroper Flüssigkeiten in magnetischen und elektrischen Feldern; Structure et Forme des Molécules, Hypothèse et Réalité; Determination of Size and Distribution of Size of Particle by Centrifugal Methods».

Svedbergs lärjungars arbeten belysa naturligtvis också hans arbetsväg. Några ha redan nämnts. Arne Westgren, som sedermera övergick till kristallkemi, enkannerligen metallernas på röntgenografisk bas, började som kolloidkemist. Han studerade i ett av de båda rummen ovanpå »kvantis» problemet om

kolloidernas osmotiska tryck, genom mätning av kolloidpartiklarnas kinetiska energi. Arbetena mynnade ut i gradualavhandlingen »Untersuchungen über die Brownsche Bewegung, besonders als Mittel zur Bestimmung der Avogadroschen Konstante», försvarad 1915.

Westgren var amanuens 1913, men blev i sin egenskap av reservlöjtnant inkallad vid världskrigets utbrott och ersattes då av Virgin, som alltså under en kortare tid på nytt blev amanuens (»kvalis»). Han var då nyligen återkommen från sin vistelse som Liljewalchsk stipendiat hos Treadwell i Zürich och Pregl i Graz. Det senare besöket gav honom möjligheten att introducera de mikrokemiska analysmetoderna i Sverige, för vilka Widman sedan fattade stort intresse. Pregl fick 1923 nobelpris. Under denna sin »come back» som amanuens bodde Virgin i det av råttor aldrig övergivna Lilla Kemikum, där även Collenberg bodde under sin amanuenstid. Att det ej endast var råttor, som trivdes visar följande bild från ett av rummen.

Efter sin disputation lämnade Westgren Upsala för en tid och fortsatte sina kolloidkemiska studier hos Zsigmondy i Göttingen. Han och författaren hade disputerat med tre dagars mellanrum. I det oförgätligt trevna lilla »Gartenhäuschen» hos alla tiders Pensionsmutter, norskan Olga Norrmann, Friedländerweg 8, förenades på nytt våra stigar, då även tillsammans med den några år senare bortgångne Gillis P:son Wetter.

Ivar Nordlunds arbetsplats var förlagd till ett av rummen ovanpå föreläsningssalen eller rättare över förrummen till denna sal. Han studerade med utgångspunkt från Svedbergs doktorsavhandling de i många avseenden speciellt intressanta kvicksilverhydrosolernas framställning och egenskaper. Undersökningarna sammanfattades i den postumt utgivna gradualavhandlingen »Experimentelle Studien über Quecksilberhydrosole, die aus metallischem Quecksilber hergestellt sind» (1918). Någon disputation blev det nämligen aldrig. Han hade strax förut lämnat Kemikums krets för alltid (1918).

Då vi tänka tillbaka på vår vän Kivet, så minnas vi väl honom mest som den pålitlige, kanske litet omständlige hedersmannen och kamraten och som den oförliknelige fotografen, som nästan gjorde kameran till en pensel. Då han och jag sommaren 1912 gjorde en studieresa till ett flertal europeiska

En afton i amanuensdubbletten på Lilla Kemikum 1916. Fr. v. S. Bodforss, N. Pihlblad, E. Söderbäck, O. Collenberg, D. Strömholm. Foto: I. Nordlund.

länder, kunde det iblandd bli litet tragikomiska intermezzon på grund av allt fotograferande. Kivet hade med sig flera olika kameror med olika användbarhet och stora och små. Jag minns en gång i Schweiz, när han under ett tåguppehåll funnit en värdig utsikt, tagbar från själva stationen. Efter mycket manipulerande var det nästan klart med stativ och allt. Då blåste tåget, och »grunkorna» fick i en hast utan att ha trätt i funktion hyvas in. Dess bättre begrep ej stinsen Kivets speciella uttryck: »Å de va de' råaste.» Vid uppstaplandet i kupén hade en tung pjäs kommit att placeras litet ostadigt. Vid ett ryck av tåget trillade den ner. Rätt på pipan av en gemytligt rökande tyrolare. Kivet var gruvligt generad, men ännu ej helt invand med tyskan, gick han fram och bockade sig artigt och sade: »Bitte sehr».

Nils Pihlblad hörde som sagt, också till den första lärjungekretsen omkring jubilaren. Han var gammal i gården på Kemikum, när han började licentiera. Hans amanuensår i olika funktioner ha redan nämnts. Doktorsarbetet, som länkade in honom på hans blivande industriella bana som teknisk

kemist och fabrikschef utfördes i den ävenledes redan nämnda *camera obscura* bakom föreläsningssalen. Pihlblad bodde, innan han tog sin nya dubblett i besittning på Gamla Kemikum. På den tiden låg den ovanpå Knut Ångströms våning, och den litet ljudkänslige professorn lär ha varit glad, då kandidat Pihlblad avflyttade och det kom en annan, som försiktigare satte ned kängorna på golvet, då sängdags var inne.

Fredrik Jansson (Jahn), omkring 1912 biträdande amanuens, arbetade i samma rum som Nordenson och avlade sin licentiatexamen 1913, varefter han gav sig ut på sin tekniskt kommersiella bana. Vid sin död (1940) var han sedan flera år verkställande direktör i Svenska Pappersbruksföreningen. Under hans tid genljöd Kemikum av en mera kvalificerad sång än den gamla kvantiskörens. Han var en av O. D:s allra bästa förmågor, och då han sjöng sina operaarior, tystnade gärna andra ljud. Widman, som inte bara var Farbror på Kemikum utan även i O. D., avbröt sin berömda kristallisationsmarsch, under vilken han, taktfast stampande i golvet och skakande ett provrör i vardera handen med någon organisk smet, medelst besvärjelsen »djäkla förbannade skit, som inte vill kristallisera», sökte framtvinga en bättre ordning, kristallografiskt betraktat. Nere i »Lejonkulan» tror jag däremot, att den hastiga promenaden runt laborationsbordet snarare blev ännu livligare, om möjligt.

Det var den tidens »ultraljudeffekter» på Kemikum. Bäst minnas vi väl Fredrik, när han icke minst till de serverande systrarnas förtjusning vid något »symposion» tog upp sitt bravurnummer, Karlfeldts Aspåkerspolska:

»Varför sitta vi så still och tysta?
Ha vi uttömt alla kära ord?
Äro alla de små läppar kyssta,
som gå leende kring detta bord?»

Yngve Björnståhl blev magister 1913 och påbörjade således sina licentiatlaborationer alldeles i slutet av det skede — jubilarens tredje och Nya Kemikums första decennium — till vilket dessa minnen anknyta sig. Han betraktade på grund av en svår sjukdom med rätta livet såsom något skäligen brutalt. Och han hade säkert också en känsla av att hans

kontakt därmed icke skulle bli alltför långvarig. Konsekvent extraherade han ut och absorberade av livet, vad som syntes honom kunna göra det njutbarare. Han blev en fragil gestalt med utpräglat sinne för det deliciösa och nobla. Sådan blev hans vetenskapliga insats, och sådan var hans smak och hans humor.

På Kemikum voro hans undersökningar förlagda till de fysikalisk-kemiska rummen, där hans första arbeten berörde problem om anisotropa vätskors egenskaper. Doktorsarbetet av 1924 hade titeln »Experimental Studies on the Accidental Double Refraction in Colloids with Special Reference to the Structure of the Colloid Particle». Under åren 1918—25 var han amanuens och den sista innehavaren av Pihlbladska dubbletten, liksom Söderbäck av den Sandqvistska. Amanuensbostäderna upphörde år 1930, enär utrymmena genom det med åren stegrade kravet på specialinredda rum togos i anspråk direkt för institutionsarbetet. Krámståhl, som vi ibland med välvillig karikatyr kallade honom — det skulle kanske ännu hellre stavas Crámståhl — blev docent och uppehöll undervisningen i fysikalisk kemi 1923, då Svedberg var professor i kolloidkemi vid Wisconsin University, och inlade vid inredandet av den nya institutionen för fysikalisk kemi utomordentliga förtjänster. Hans bok »The New Laboratory of Physical Chemistry at Upsala University» bär vittne härom. Han avled 1942.

Denna bild av institutionslivet under en uppenbar brytningsperiod i kemins utveckling skulle förvisso vara ofullständig, om ej föreläsningsverksamheten i korthet berördes. Den talar sitt tydliga språk. Av professorliga lärostolar fanns det vid den nya institutionens öppnande endast en: Widmans. Snart tillkom även Strömholms och efter ytterligare några år Svedbergs. Widman föreläste alternerande en lägre kurs, det vill säga helt enkelt den elementära lärobokens pensum, och en högre kurs med valda delar från hans arbetsområde inom organisk kemi. Strömholm gav på samma sätt en på den tiden högst välbehövlig översikt över den analytiska kemins teori på dissociationsteoretisk grund. Det var under en av dessa föreläsningar, han oavsiktligt fällde det ofta citerade uttrycket: »Vattnets dissociationskonstant är oändligt liten, det vill säga ändå inte så liten utan i själva verket ganska stor». Han kom

nämligen plötsligt att tänka på vattnets inverkan på vissa jämviktsförhållanden. Han kunde med gott samvete sagt så med avsikt, ty formuleringen gav en förträfflig bild av hydrolysen, som man både begrep och kom ihåg. Den kan ställas vid sidan av fysikern Gustaf Granqvists (»Grankulans») lika målande och lika bekanta tes »de flesta kroppar utvidga sig vid temperaturförhöjning, men det finnes också de, som ha negativ utvidgningskoefficient, nämligen de, som sammandraga sig när de utvidga sig». Ack, hur många grodor kunna ej hoppa ur munnen på en föreläsare, men hur många kväka ett så begripligt språk!

Strömholms valfria föreläsningar gåvo belysande framställningar från olika områden av kemin, och han avlägsnade sig där gärna från de komplexföreningar och jämviktsproblem, som han experimentellt bearbetade. Då jag plockar ned mina kollegiehäften från den tiden, finner jag t. ex. följande: *Katalys*, ett område, där det på den tiden var betydligt värre att ur litteraturen få fram ett sammanhang än nu, sedan Langmuir och andra givit det teoretiska underlaget. Vidare *Werners koordinationslära* och *Nyare atomviktsbestämningar*, så upplagt, att en hel del kunskap om de ifrågavarande ämnenas icke så lättåtkomliga kemi meddelades.

Svedberg började som docent föreläsa redan 1910 och fortsatte naturligtvis senare även som professor. I anteckningarna återfinnas *Kolloidkemi*, *Radioaktivitetslära*, *Materiens struktur*, *Affinitetslära*, *Nya undersökningar om molekylers och atomers struktur* och *Fotokemi*. Det var en ny sorts kemi, som öppnade sig för oss, där vi funno, att en kemist fick lov att lära sig handskas med andra instrument än våg, degel och fraktionerkolv.

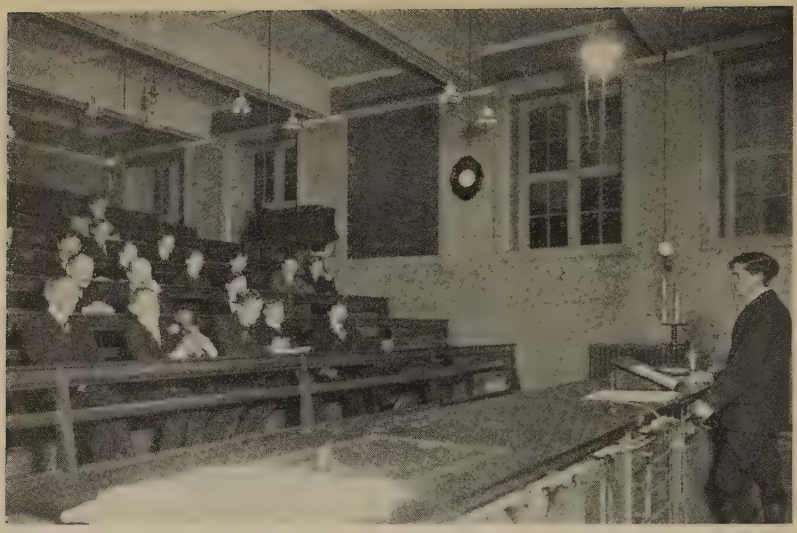
Men det var nu icke endast av det ord, som utgick *ex cathedra*, som vi levde. Det fanns, som redan nämnts, också något, som hette Kemiska Sektionen eller rättare: Sektionen för kemi och mineralogi av Naturvetenskapliga Studentsällskapet, vilket också hade sektioner för botanik, zoologi och geologi. Fysiska Sällskapet levde för sig självt, liksom de övriga Sällskapen nu göra. Sektionssystemet tycks vara borta.

Denna Kemiska Sektion spelade i de dagarnas vetenskapliga liv, liksom också tidigare, en högst betydande roll. Under »vår tid» höllos sammanträden i regel varannan fredag under

normal terminsperiod, först på det så kallade »sektionsrummet», där senare Odén och de andra fysikaliska kemisterna arbetade, och senare på den vanliga stora föreläsningssalen. Naturvetenskapliga Studentsällskapet hade en ordförande. Inom sektionerna fungerade sekreteraren samtidigt som sådan. Förutom honom funnos de vanliga föreningsfunktionärerna samt referenter för olika kemiområden. Bläddrar man i protokollsböckerna, så återfinner man från posten som klubbmästare och uppåt till sekreterarens höjdplatå de flesta av de personer, som i det föregående ha nämnts. Böckerna innehålla ett icke föraktligt kapitel svensk kemihistoria.

Svedbergs namn möter man första gången i berättelsen från sammanträdet den 29 september 1904, då han valdes till referent. Sekreterare blev han vid motsvarande sammanträde 1907. Mycket flitiga föredragshållare voro under 1900-talets allra första år Daniel Strömholm, Carl Benedicks och Arvid Odencrantz, i all synnerhet den senare, som talade om de fotografiska processernas förlopp. Benedicks uppehöll sig naturligtvis i första hand vid metallernas fysikaliska kemi, men hans intresse för historisk kemi skymtar ej sällan. Strömholms föredrag handla oftast om komplexkemi och användningar av fasläran. I sitt föredrag den 4 december 1908 redogjorde han för sina tillsammans med Svedberg utförda undersökningar av radioaktiva toriumelement. Genom fortsättningen av dessa arbeten framkom uppslaget till begreppet isotopa element (1909).

Rent analytiskt kemiska föredrag förekommo ofta under denna tid, t. ex. av Naima Sahlbom om nyare metoder inom silikatanalysen. Oskar Widman lämnade som docent och under sina allra första år som professor ej sällan meddelanden från sina organiskt syntetiska arbeten, och H. von Euler och S. Schmidt-Nielsen skötte om kontakten med mer eller mindre direkt biokemiska frågor. Det periodiska systemet synades då och då i sömmarna, och det hände under denna tid, då dess djupaste innebörd ännu länge skulle vara fördold, att mer eller mindre mystiska talförhållanden och regelbundenheter debatterades. Vi minnas nog alla Seth Roséns föredrag den 5 oktober 1908 och den ytterst livliga diskussion, som därefter följde. Radioaktivitet och röntgenstrålar stå självfallet ofta på föredrags- och referensprogrammen, och framför allt via



T. Svedberg håller föredrag i kemiska sektionen 1915. Fr. v. E. Söderbäck, N. Pihlblad (med Almströms hund Tommy), J. A. Hedvall (sekr.), H. Sandqvist, G. K. Almström, O. Holmberg, N. von Zweigbergk, H. Rinde, A. Westgren, H. Nordenson, därefter några kurslaboranter och längst bak H. Gad. Foto: I. Nordlund.

dessa gemensamma intressen uppehölls förbindelsen med Fysiska Sällskapet.

Det är nästan överraskande att finna, att tekniska problem ej så sällan togos upp under denna tid, som ej oberättigat fått namn om sig att ej vårda sig mycket om broslagning över klyftan mellan teori och tillämpning. Hellsing redogjorde för sina och andras arbeten med oljeutvinning ur den svenska skiffern och Rinman för sina undersökningar av framställning av trämassa och biprodukter vid vedens kokning med rent alkali.

Samarbete med den medicinska kemin existerade, och det var naturligtvis framför allt genom Carl Thore Mörner, kemisten bland medicinarna och kemist också till själen. Calle Mörner hade sitt analytiska »referenslaboratorium» i munnen. Han smakade faktiskt på precis vad som helst och avgav sitt utlåtande.

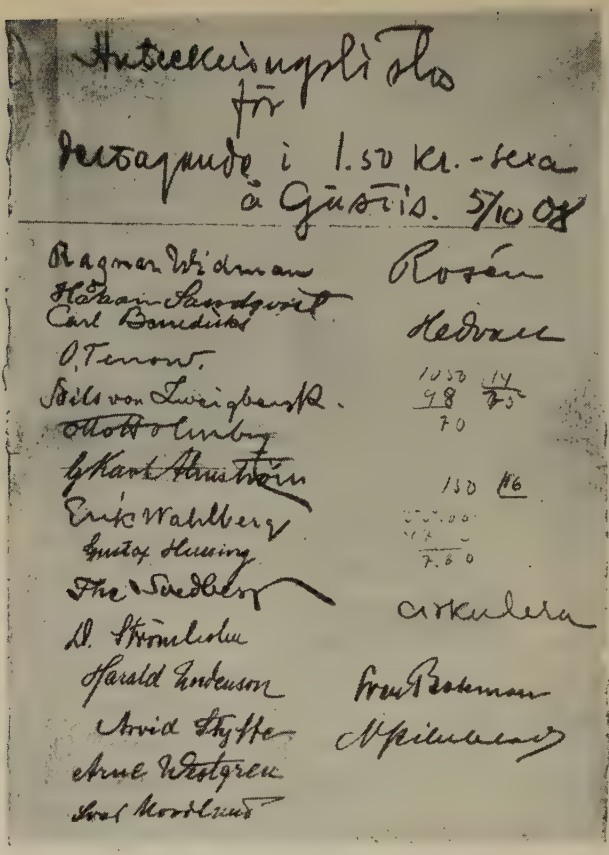
Kontakten med de andra sektionerna av Naturvetenskapliga Sällskapet var mer eller mindre god. Med geologer och mineraloger det förra. Artur Bygdén, Per Geijer, Ragnar Loo-

ström, Percy Quensel och Nils Zenzén voro inga främlingar hos oss och vi icke hos dem. En del av dem voro ju för övrigt både kemister och geologer, och om den dåvarande lektorn vid Ultuna, sedermera professor vid Stockholms Högskola, K. A. Vesterberg (död 1927), kan man väl också säga detta.

Något givande utbyte med botanister och zoologer existerade väl knappast annat än »kohandeln» vid Linnéstipendiernas utdelande. I det avseendet var det på den tiden dåligt med bryggor och broar. Man levde nog ännu till en viss grad i isolationens tecken, och det var säkert icke många, som ens hade reda på vad kemisterna vid systeruniversitetet i Lund hette och gjorde. Intet under då att kontakten med botaniken och zoologin var dålig. I avseende på den förra fanns dock ett lysande undantag. Det hette som vanligt The Svedberg, vilken redan då var botanist långt över det vanliga växtsamlandets nivå. Vi veta, att han nu bär ett internationellt känt namn även på detta område. Den som haft glädjen vandra med honom på det underbara Vretaudd utanför Upsala vid Mälaren, kan inte låta bli att tänka på Hammarby och den kärlek, som där kom Floras barn att trivas. Med samma ömhet ansar han under sommarmånaderna också sina skyddslingar på hans efter *Glaucium flavum* uppkallade Flava utanför Fjällbacka eller på de fridlysta Vassholmarna. Då man ser frodigheten hos den där växande *Mertensia maritima* och den mjuka mattan av *Ammodenia peploides* är man nästan böjd att tro på ett rent personligt inflytande på växtligheten.

Till zoologerna kröp Kemiska Sektionens förhållande nog under nollstrecket efter en natriumfest borta i Norbyskogarnas vattenpölar. Det var så, att hela förrådet av organikernas tillvaratagna »natriumspaghetti» brukade bevaras till sista »vårsektionen», då det kastades i en av de nämnda små dammarna. Blixt och dunder! Och naturligtvis blev vattnet alkaliskt. Men att detta kunde innebära några nackdelar för någon, hade ju ingen tänkt på. Ett år råkade emellertid en ung zoolog odla några små kreatur i bemälda damm i studiesyfte. De lära efter natriumbehandlingen ha företett genomgripande förändringar, som inte riktigt hörde till programmet.

The lät höra sig i Sektionens kateder första gången den 31 oktober 1905. Boken förmäler därom, att »Kand. The Sved-



En anteckningslista till »postsektion».

berg höll ett längre föredrag om kolloidala kroppar». Den 20 september 1906 gav han en redogörelse för resultat av egna undersökningar, så som fallet var och förblev bland de på institutionen vetenskapligt arbetande. Därmed började en av amanuensen, licentiaten, docenten och professorn The Svedberg given lång rad av meddelanden och föredrag. Frikostigt och utan skymt av hemlighetsmakeri delade han med sig av sina olika rön, entusiasmerade auditoriet och förvärvade lärjungar. Och efteråt var han gärna med på »postsektionen», vilket t. ex. framgår av vidstående bild av en från min sexmästartid bevarad anteckningslista. Plötsligt kunde han emellertid vara försvunnen, och de, som hade sin väg till Kemikum, funno att det

arbetades mitt i natten i de Svedbergska laboratorierummen, där han tidvis hade en sovbrits.

Ofta märkte åhörarna, att hans intresse gick långt utöver den rena grundforskningen. Han inflickade gärna tillämpningssynpunkter i sina anföranden. Då jag lämnat Kemikum och hade en industriell anställning fjärran från Upsalakretsen, skrev jag i något ärende till The och uttryckte väl min saknad av allt och alla, som voro mig från den tiden kära. Hans svar (1917), tydligen nedskrivet i ett ögonblick, då sinnet var trött vid teoretiserande, kan ha sitt intresse som bakgrund till den eminenta betydelsen även för tekniskt och praktiskt liv, som hans forskning redan då naturligtvis hade men framförallt senare erhållit, lydde: »Bror klagar dumt. Vi här trassla in oss i ofruktbara dillerier. Bror är blifven en nyttig människa — hvilket man svårligen kan säga om oss.»

Käre The, min vävstol har stannat. För oss alla lysa säkert våra minnen från denna kemikumtid som en ädel gobeläng. Men skytteln löper olika i olika vävares händer. Relief och färgintryck bero därav. Men om konturerna ej äro för skarpt dragna, kan betraktaren kanske se den bild han helst vill ha fram. Då flyta hågkomsterna vidare av sig själva och varp och väft, ord eller färger, bli endast en hjälp till deras individuella begagnande. Kanske kunna dessa blad spela den rollen.

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Index of Authors.

Page

ADELL, B., Docent, Kemiska Institutionen, Lund 33

ADLER, E., Dr.-Ing., Institutet för Organisk-Kemisk Forskning, Stockholms Högskola, Stockholm 246

ALM, C. G., Amanuens, Botaniska Institutionen, Uppsala 578

ANDERSSON, K. J. I., Fil. Mag., Forskningslaboratoriet LKB, Alvik, Stockholm 11

ARRHENIUS, S., Docent, Fysikalisk-Kemiska Institutionen, Uppsala . . 419

BODFORSS, S., Professor, Kemiska Institutionen, Lund 33

BORGMAN, K., Ingenjör, Fysikalisk-Kemiska Institutionen, Uppsala . . 429

BROHULT, S., Docent, Forskningslaboratoriet LKB, Alvik, Stockholm 429, 623

BRUNO, C. A., Fil. Mag., Avdelningschef, Dagens Nyheters Grafiska Avdelning, Stockholm 65

BÄCKSTRÖM, H. L. J., Docent, Institutionen för Allmän och Oorganisk Kemi, Stockholms Högskola, Stockholm 45

BÄCKSTRÖM, H., Docent, Fotografiska Institutionen, Kungl. Tekniska Högskolan, Stockholm 65

CLAESSON, S., Fil. Lic., Fysikalisk-Kemiska Institutionen, Uppsala . . 82

DAHLÉN, A., Tekn. Dr., A.B. Bofors, Nobelkrut, Bofors 234

DRUCKER, C., Professor, Fysikalisk-Kemiska Institutionen, Uppsala . . 94

EKWALL, P., Professor, Fysikalisk-Kemiska Institutionen, Åbo Akademi, Åbo, Finland 104

ENEBO, L., Civilingenjör, Laboratoriet för Jäsningslära, Kungl. Tekniska Högskolan, Stockholm 438

ENGBLOM, A., Överingenjör, Borås Wäfveri A.B., Borås 639

VON EULER, H., Professor, Institutet för Organisk-Kemisk Forskning, Stockholms Högskola, Stockholm 246

FREDGA, A., Professor, Kemiska Institutionen, Uppsala 261

GARD, S., Docent, Fysikalisk-Kemiska Institutionen, Uppsala 530

GRALÉN, N., Docent, Svenska Textilforskningsinstitutet, Göteborg 274, 623

GROTH, B. S., Fil. Dr., Kemiska Forskningslaboratoriet, Mo och Domsjö A.B., Örnsköldsvik 288

GRÖNWALL, A., Docent, Fysikalisk-Kemiska Institutionen, Uppsala . . 540

HEDVALL, J. A., Professor, Institutionen för Kemisk Teknologi, Chalmers Tekniska Högskola, Göteborg 113, 681

HEVESY, G., Professor, Vitamininstitutet, Stockholms Högskola, Stockholm 456

HOLMBERG, B., Professor, Kungl. Vetenskapsakademiens Organisk-Kemiska Laboratorium, Stockholm 299

Page
HÄGG, G., Professor, Kemiska Institutionen, Uppsala 140
INGELMAN, B., Fil. Mag., Fysikalisk-Kemiska Institutionen, Uppsala . 155
JOHANSON, S. B. H., Civilingenjör, Kemiska Forskningslaboratoriet, Mo och Domsjö A.B., Örnsköldsvik 288
JULLANDER, I., Fil. Lic., Fysikalisk-Kemiska Institutionen, Uppsala . . 166
JUUP, G., Diplomingenjör, Fysikalisk-Kemiska Institutionen, Åbo Akademi, Åbo, Finland 104
LAMM, O., Docent, Fysikalisk-Kemiska Institutionen, Uppsala 182
LARSSON, E., Professor, Organisk-Kemiska Institutionen, Chalmers Tekniska Högskola, Göteborg 311
LIANDER, H., Överingenjör, ASEA, Västerås 320
LUNDIN, H., Fil. Dr., A.B. Stockholms Bryggerier, Stockholm 438
MONNÉ, L., Dr. Phil., Wenner-Grens Institut, Stockholms Högskola, Stockholm 500
MOSIMANN, H., Dr. Phil., Fysikalisk-Kemiska Institutionen, Uppsala . 464
MÜLLER, M., Förste Assistent, Fotografiska Institutionen, Kungl. Tekniska Högskolan, Stockholm 65
MYRBÄCK, K., Professor, Institutionen för Organisk och Biokemi, Stockholms Högskola, Stockholm 474
NANNFELDT, J. A., Professor, Botaniska Institutionen, Uppsala . . . 601
NILSSON, P. E., Assistent, Mikrobiologiska Institutionen, Lantbrukshögskolan, Uppsala 484
NILSSON, R., Professor, Mikrobiologiska Institutionen, Lantbrukshögskolan, Uppsala 484
NORDENGREN, S., Direktör, A.B. Förenade Superfosfatfabriker, Landskrona 113
NORDENSON, H., Fil. Dr., Liljeholmens Stearinfabriks A.B., Stockholm 659
NORIN, R., Docent, Höganäs-Billesholms A.B., Höganäs 189
OLSSON, J., Ingenjör, Stockholms Superfosfat Fabriks A.B., Ljungaverk 344
OLSSON, N., Professor, Husdjursförsöksanstalten, Lantbrukshögskolan, Uppsala 484
PEDERSEN, K. O., Fil. Lic., Fysikalisk-Kemiska Institutionen, Uppsala 490, 523
QUENSEL, O., Fil. Dr., Försvarsväsendets Kemiska Anstalt, Stockholm 193
RUNNSTRÖM, J., Professor, Wenner-Grens Institut, Stockholms Högskola, Stockholm 500
RÄNBY, B., Fil. Kand., Fysikalisk-Kemiska Institutionen, Uppsala . . 274
SIGNER, R., Professor, Chemisches Institut, Universität Bern, Schweiz 464
SJÖGREN, B. Laboratoriechef, A.B. Astras Centrallaboratorier, Södertälje 547
SMITH, L., Professor, Kemiska Institutionen, Lund 352
SNELLMAN, O., Docent, Fysikalisk-Kemiska Institutionen, Uppsala 200, 530
STENHAGEN, E., Docent, Medicinsk-Kemiska Institutionen, Uppsala . . 11
STÄLLBERG-STENHAGEN, STINA, Med. Kand., Medicinsk-Kemiska Institutionen, Uppsala 11
SUNNER, S., Fil. mag., Kemiska Institutionen, Lund 352

Page

Svensson, H., Fil. Lic., Fysikalisk-Kemiska Institutionen, Uppsala . . 213
Säverborn, S., Fil. Lic., Fysikalisk-Kemiska Institutionen, Uppsala . 508
Theorell, H., Professor, Medicinska Nobelinstitutets Biokemiska Avdelning, Karolinska Institutet, Stockholm 523
Tiselius, A., Professor, Fysikalisk-Kemiska Institutionen, Uppsala . . 370
Tyrén, H., Fil. Mag., Fysikalisk-Kemiska Institutionen, Uppsala 224, 530
Ulfsparre, S., Civilingenjör, Domsjö Sulfitfabrik, Örnsköldsvik . . . 379
Waldenström, J., Docent, Medicinska Kliniken, Akademiska Sjukhuset, Uppsala 558
Waller, A., Civilingenjör, Uddeholms A.B. Skoghallsverken, Skoghall 400
Westgren, A., Professor, Kungl. Vetenskapsakademien, Stockholm . . 665
Widström, G., Med. Dr., Serafimerlasarettet, Stockholm 574
Winbladh, R., Tekn. Dr., Centralbolaget för Kemiska Industrier A.B., Stockholm 675
Öhman, V., Ingenjör, Nitroglycerin A.B., Gyttorp 413

Abbreviations of periodicals cited in this volume have been made according to the standard adopted by the International Union of Chemistry (see "List of Periodicals Abstracted", Chemical Abstracts, American Chemical Society, Vol. 30, 1936).

Contents.

Page

Introduction 3

A Recording Surface Balance of the Wilhelmy-Dervichian Type. By K. J. I. Andersson, S. Ställberg-Stenhagen and E. Stenhagen 11

Über lichtelektrische Extinktionsmessungen mit Hilfe von Multiplikatorzellen. Von S. Bodforss und B. Adell . . 33

The Photochemical Oxidation of Alcohols in the Presence of Benzophenone. By H. L. J. Bäckström 45

Investigation of the Photographic Latent Image by Means of the Pressure Effect. By H. Bäckström, C. A. Bruno and M. Müller 65

A Self-Registering Apparatus for Adsorption Analysis. By S. Claesson 82

Über die Grösse von Flüssigkeitsmenisken. Von C. Drucker 94

Die potentiometrische Fällungstitration von hochmolekularen Fettsäuren mit Silbernitrat. Von P. Ekwall und G. Juup . . 104

Framställning av kalisalter ur svensk råvara. Av J. A. Hedvall och S. Nordengren 113

Optically Active Organic Molecules in Crystal Lattices. By G. Hägg 140

Méthode dilatométrique pour étudier la vitesse de cristallisation de solutions sursaturées de sucre. Par B. Ingelman . 155

Über die Berechnung von Molekulargewichten polymolekularer Substanzen aus Messungen von Sedimentationsgeschwindigkeit und Diffusion. Von I. Jullander 166

The Theory of Sedimentation Equilibrium and the Determination of a Thermodynamic Factor Occuring in the General Diffusion Equation. By O. Lamm 182

Experiments in Calculating the Actual Mineralogical Composition of Ceramic Silica Bricks by the Aid of Differential Thermal Analysis. By R. Norin 189

A Method for the Determination of Diffusion Constants. By O. Quensel 193

Beitrag zur Kenntnis der Theorie des elektrooptischen Effectes in Kolloiden. Von O. Snellman 200

Some Aspects of Preparative Electrophoresis. By H. Svensson 213

A Neutron Generator for Preparative Use. By H. Tyrén . . 224

Page

On the Development and the Use of the Aryl Sulphonamide Resins. Especially of Those Built Upon p-Toluene Sulphonamide. By A. Dahlén 234
Über α, β-Dialkyl-stilbenchinone, neue synthetische Östrogene. Von H. v. Euler und E. Adler 246
On the Use of Melting Point Curves for the Establishment of Steric Relationships Between Optically Active Compounds. By A. Fredga 261
High-Molecular Wood Celluloses. By N. Gralén and B. Rånby 274
Production of Vinyl Acetate from Acetylene and Acetic Acid in the Presence of the Mercury Salts of Complex Fluorine Acids. By B. S. Groth and S. B. H. Johanson 288
Thiobenzoylaminosäuren. Von B. Holmberg 299
Zur Kenntnis der Komplexbildung zwischen Silber und einigen schwefelhaltigen Karbonsäureionen in wässeriger Lösung. Von E. Larsson 311
Wire Enamels. By H. Liander 320
Melamine and Melamine Resins. By J. Olsson 344
Verbrennungen von chlor- und bromhaltigen Substanzen in beweglicher Bombe. Von L. Smith und S. Sunner . . . 352
Quantitative Adsorption Analysis of Some Amino Acid and Peptide Mixtures on Active Carbon. By A. Tiselius . . 370
On the Chemistry of Sulphite Cellulose Cooking. By S. Ulfsparre 379
On Wood Cellulose as a Raw Material in Chemical Industry. By A. Waller 400
An Example of the Use of Adsorption Analysis in Technical Synthesis. By V. Öhman 413

A Dielectric Investigation of Serum Proteins Treated with Alcohol and Ether. By S. Arrhenius 419
L'hémocyanine de *Helix pomatia* est-elle composée de deux espèces de molécules? Par S. Brohult et K. Borgman . 429
On the Fermentation of Cellulose and Similar Carbohydrates by Thermophilic Bacteria. By L. Enebo and H. Lundin . 438
Retention of Atoms of Maternal Origin in the Adult White Mouse. By G. Hevesy 456
Sedimentationsgleichgewichte und molekulare Konstitution von Gelatinefraktionen. Von H. Mosimann und R. Signer . . 464
The Constitution and Enzymatic Degradation of Starch and Glycogen. By K. Myrbäck 474
Penicillium notatum als Ausgangsmaterial bei der Darstellung von Vitamin D_2. Von R. Nilsson, N. Olsson und P. E. Nilsson 484

Page

Fetuin, a New Globulin Isolated from Calf Serum. By K. O. Pedersen 490
Cytoplasmic Structure of the Sea Urchin and Starfish Egg. By J. Runnström and L. Monné 500
On the Molecular Weight of Gum Arabic. By S. Säverborn 508
The Molecular Weight and Light Absorption of Crystallized Lactoperoxidase. By H. Theorell and K. O. Pedersen . 523

Studies on Macromolecular Components in Faeces and Intestinal Contents. By S. Gard, O. Snellman and H. Tyrén . . 530
An Attempt at Physico-chemical Analysis of Protein Antigens Isolated from the Tubercle Bacillus. By A. Grönwall . . 540
Sulphanilamides and Experimental Tuberculosis. Some New Approaches. By B. Sjögren 547
Signs and Causes of Clinical Hyperglobulinemina. By J. Waldenström 558
Some Comments on the Large Scale Production of Transfusion Plasma. By G. Widström 574

Om *Carex macloviana* d'Urv. och dess utbredning i Nordeuropa. Av C. G. Alm 578
Orchis strictifolia Opiz var. *ochroleuca* (Boll) Hyl., en förbisedd svensk kalkkärrväxt. Av J. A. Nannfeldt 601

The Institute of Physical Chemistry at the University of Uppsala. By S. Brohult and N. Gralén 623
Research and Progress in the Textile Industry. By A. Engblom 639
Reflections on Scientific Research and Industrial Development. By H. Nordenson 659
Anders Gustaf Ekebergs kemiska föreläsningar. 1805—1811. Av A. Westgren 665
Science and Chemical Industry in Collaboration. By R. Winbladh 675

Från Nya Kemikums första tid. Av J. A. Hedvall . . . 681

Index of Authors 726
Contents 729

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